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FORMALDEHYDE

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ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals provide detailed information on chemical substances. This information is intended to assist the reader in designing countermeasures for spills and to assess their impact on the environment. The report has been reviewed by the Technical Services Branch, Environmental Protection Service, and approved for publication. Approval does not signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute endorsement for use.

EnviroTIPS manuals are available from:

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ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

Technical Services Branch
Environmental Protection Programs Directorate
Environmental Protection Service
Ottawa, Ontario

April 1985

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FOREWORD

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals were initiated in 1981 to provide comprehensive information on chemicals that are spilled frequently in Canada. The manuals are intended to be used by spill specialists for designing countermeasures for spills and to assess their effects on the environment. The major focus of EnviroTIPS manuals is environmental. The manuals are not intended to be used by first-response personnel because of the length and technical content; a number of manuals intended for first-response use are available. The information presented in this manual was largely obtained from literature review. Efforts were made, both in compilation and in review, to ensure that the information is as correct as possible. Publication of these data does not signify that they are recommended by the Government of Canada, nor by any other group.

ACKNOWLEDGEMENTS

The final version of this manual was prepared by the staff of the Environmental Protection Service who wrote extensive revisions to the text, drafted illustrations and incorporated all comments and additions.

The level of detail present was made possible by the many individuals, organizations and associations who provided technical data and comments throughout the compilation and subsequent review. The draft of this manual was prepared under contract to Environment Canada by M.M. Dillon Consulting Engineers and Planners, Concord Scientific Corporation, and Waterloo Engineering Limited.

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1 SUMMARY

FORMALDEHYDE (HCHO)

Colourless, watery solution or gas with a pungent, irritating odour.

SYNONYMS

Pure formaldehydes: Formic Aldehyde, Methanal, Methyl Aldehyde, Methylene Oxide, Methylene Glycol, Oxomethane, Oxomethylene, Aldehyde formique (Fr.)

Solutions: Formalin, Formol, Karsan

Solid polymers: Paraformaldehyde, Trioxane

IDENTIFICATION NUMBERS

UN. No. 1198 (solution, flash point <61°C), 2209 (solution, flash point >61°C); CAS No. 50-00-0; OHM-TADS No. 7216732; STCC N0. 4940341 or 4940342

GRADES & PURITIES

Aqueous solutions, 37 to 52 percent formaldehyde by weight, 7 to 15 percent methanol (inhibited) or 1 percent methanol (uninhibited).

IMMEDIATE CONCERNS

Fire: Combustible

Human Health: Highly toxic by inhalation, ingestion and contact. Suspected carcinogen.

Environment: Harmful to aquatic life in low concentrations.

PHYSICAL PROPERTY DATA

Shipping state: (Liquid) 37 percent solution
State (15°C, 1 atm): liquid
Boiling Point: ≈97°C
Flammability: combustible
Flash Point: 56 to 85°C (CC)
Vapour Pressure: 6.3 kPa (38°C)

Density: 1.075 to 1.125 g/mL (25°C)
Solubility (in water): miscible
Behaviour (in water): mixes; no reaction
Behaviour (in air): vapours are combustible
Odour Threshold Range: 0.5 to 1.0 ppm

ENVIRONMENTAL CONCERNS

Formaldehyde is toxic to aquatic life in concentrations as low as 1 mg/L. It is not known to bioconcentrate or bioaccumulate.

HUMAN HEALTH

TLV•: 1 ppm (1.5 mg/m^3)
IDLH: 100 ppm

Exposure Effects

Inhalation: Vapour is irritating to the eyes and respiratory tract. Causes sore throat, coughing, bronchitis, nausea, gastric pain, hemorrhage and possibly death.

Contact: Contact with the skin causes irritation, tanning effect and allergic sensitization. Contact with eyes causes irritation, itching, lacrimation and possible damage in the case of large doses.

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning "COMBUSTIBLE & POISON". Call fire department and notify manufacturer. Eliminate sources of ignition including traffic and equipment. Stop the flow and contain spill, if safe to do so. Avoid contact with liquid and vapour; stay upwind of release. Keep contaminated water from entering sewers or watercourses.

Fire Control

Use alcohol foam, dry chemical, carbon dioxide, water spray or fog to extinguish. Cool fire-exposed containers with water. Containers may explode in heat of fire.

COUNTERMEASURES

Emergency Control Procedures in/on

Soil: Construct barriers to contain spill or divert to impermeable holding area. Remove material with pumps or vacuum equipment. Absorb residual liquid with natural or synthetic sorbents and shovel into containers with covers.

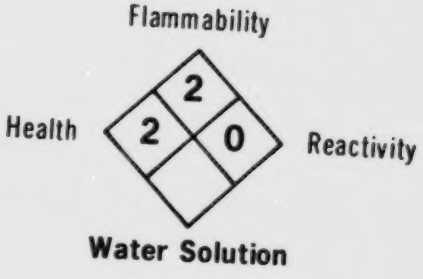
Water: Contain by damming, water diversion or natural barriers. If possible, remove contaminated water for treatment.

Air: Use water spray to knock down vapour. Control runoff for later treatment and/or disposal.

NAS HAZARD RATING

Category	Rating
Fire	2
Health	
Vapour Irritant	3
Liquid or Solid Irritant	2
Poison	3
Water Pollution	
Human Toxicity	3
Aquatic Toxicity	3
Aesthetic Effect	2
Reactivity	
Other Chemicals	2
Water	0
Self-reaction	1

NFPA
HAZARD
CLASSIFICATION



Water Solution

Gas

2 PHYSICAL AND CHEMICAL DATA

	Gas	37 Percent Aqueous Solution
Physical State Properties		
Appearance	Colourless gas (MCA 1960)	Clear colourless liquid (Celanese PB)
Usual shipping state(s)	Not commercially available (MCA 1960)	37 percent solution inhibited with 7 to 15 percent methyl alcohol or with 1 percent methanol (uninhibited) (Celanese PB)
Physical state at 15°C, 1 atm	Gas	Liquid (aqueous solution)
Melting point	-118°C (Kirk-Othmer 1980)	
Boiling point	-19°C (Kirk-Othmer 1980)	97°C (inhibited with 7 percent methanol) (MCA 1960)
Vapour pressure	101 kPa (-19°C) (CRC 1980)	6.3 kPa (38°C) (Celanese MSDS 1979)
Densities		
Density	0.8153 g/mL (Liquid at -20°C)	Methanol Content (%) / Density (20°C): 7 — 1.097; 10 — 1.089; 12 — 1.083; 15 — 1.075 (Kirk-Othmer 1980)
Specific gravity	0.815 (-20°/4°C) (Verschueren 1984)	Methanol Content (wt.%) / Specific Gravity (25/25°C): 7 — 1.098; 10 — 1.088; 12 — 1.083; 15 — 1.075 (MCA 1960)

	Gas	37 Percent Aqueous Solution
Vapour density	1.075 (MCA 1960) 1.067 (Ullmann 1975)	1.03 (approx.) (MCA 1960)
Fire Properties		
Flammability	Flammable gas (NFPA 1978)	Gas vaporizes readily from solution and is flammable in air (NFPA 1978)
Flash point		Methanol Content (wt.%) / Flash Point (CC): 1 — 85°C 7 — 72°C 10 — 64°C 12 — 60°C 15 — 56°C (MCA 1960; CCPA 1983)
Autoignition temperature	424°C (NFPA 1978) 430°C (Kirk-Othmer 1980)	
Upper flammability limit	73 percent (v/v) (NFPA 1978)	
Lower flammability limit	7.0 percent (v/v) (NFPA 1978)	
Heat of combustion	571 kJ/mole (20°C) (CRC 1980)	
Combustion products	Carbon dioxide and water (CRC 1980)	
Other Properties		
Molecular weight	30.03 (CRC 1980)	
Constituent components of typical commercial grade	-	37.25 ± 0.25 percent formaldehyde: inhibited, 6.5 to 15 percent methanol; uninhibited, 0.5 to 1.5 percent methanol (Celanese PB)

	Gas	37 Percent Aqueous Solution
Viscosity	0.32 mPa·s (Liquid at -40°C)	Methanol Content (%) / Viscosity (mPa·s) (20°C): 1 / 2.05; 7 / 2.20; 10-15 / 2.50 (Kirk-Othmer 1980)
Refractive Index	0.0814 mPa·s (Vapour at 25°C) (PPH 1984)	Methanol Content (%) / Refractive Index (18°C): 1 / 1.37586; 7 / 1.37654; 10-15 / 1.37688 (Kirk-Othmer 1980)
Latent heat of vaporization (at boiling point)	24.76 kJ/mole (CRC 1980)	
Heat of formation	-115.9 kJ/mole (25°C) (JANAF 1971)	
Entropy	218.8 J/(mole·K) (Ullmann 1975)	
Ionization potential	10.88 eV (Hernandez 1977)	
Heat of solution	-62 kJ/mole (Ullmann 1975)	
Heat of polymerization	63 kJ/mole (Kirk-Othmer 1980)	
Heat Capacity Constant pressure (C_p) (25°C)	35.4 J/(mole·°C) (JANAF 1971)	
Critical pressure	6637 kPa (Kirk-Othmer 1980)	
Critical temperature	141.2°C (Kirk-Othmer 1980)	
Coefficient of thermal expansion	0.00283/°C (Gas at 25°C) (Ullmann 1975)	0.0005 to 0.0006/°C (Celanese PB)

	Gas	37 Percent Aqueous Solution
pH of aqueous solution	-	2.8 to 4.0 (Merck 1976)
Log_{10} Octanol/water partition coefficient	-0.87 (NRC 1981)	
Thermal Conductivity	1.59×10^{-4} W/(cm·K) (Gas at 25°C), 2.68×10^{-3} W/(cm·K) (Liquid at -40°C) (PPH 1984)	
Solubility		
In water	Soluble (CRC 1980)	Miscible (Merck 1976)
In other common materials	Soluble in diethyl ether, acetone and benzene. Soluble in ethanol and chloroform (CRC 1980)	Miscible in ethanol and acetone (Merck 1976). Soluble in methanol, butanol and propanol (Celanese PB)
Vapour Conversion Factor	1 ppm = 1.248 mg/m^3 (20°C) (Verschueren 1984)	

Chemical and Physical Properties (Kirk-Othmer 1980; NRC 1981; Ullmann 1975)

Formaldehyde. Formaldehyde is a gas at ordinary temperatures and pressures; due to its ability to polymerize, it is not available commercially. The tendency to polymerize decreases with increasing temperature. Above 400°C, the gas decomposes by either of the following two reactions:

$$2HCHO \rightarrow CH_3OH + CO$$
$$HCHO \rightarrow CO + H_2$$

In aqueous systems or as a vapour, formaldehyde readily oxidizes to formic acid. The latter is also a major metabolic product in organisms. In solution, the formic acid content increases over time. At 35°C, the formic acid content increases at 1.5-3 ppm/day and at 65°C at 10-20 ppm/day, depending on available oxygen and other conditions.

Solutions (Formalin). In aqueous solutions, formaldehyde exists as methylene glycol, polyoxymethylene ($HO-(CH_2O)_n-H$) and hemiformals. Even in concentrated

solutions, the unhydrated formaldehyde is less than 0.04 percent by weight. Formaldehyde vapour can be released continuously from a solution; this release can be increased by heating. The amount of monomeric formaldehyde present in solution can be estimated by the following:

$$\text{monomer (mole \%)} = 100 - 12.3\sqrt{F} + (1.44 - 0.0164F)\,M$$

where F = weight percent HCHO

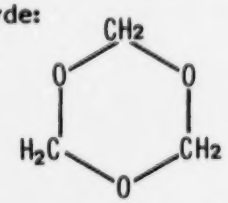
M = weight percent methanol

Polymerization occurs readily in aqueous solution; methanol and other alcohols are therefore added as inhibitors. Polymerization occurs more rapidly at lower temperatures. Formaldehyde solutions are therefore stored at temperatures above 16-21°C. Polymerization can be recognized by the cloudy appearance rendered to a normally clear solution.

Most commerce of formaldehyde is in the form of methanol-inhibited aqueous solutions.

Paraformaldehyde. Some commerce exists in a solid polymeric form known as paraformaldehyde. This substance is best represented by the formula $HO\text{-}(HCHO)_n$, where n is 8 to 100. The solid has a melting point of 120 to 170°C, depending on the state of polymerization. At room temperature, formaldehyde slowly vaporizes from the solid; however, on heating it rapidly releases monomeric formaldehyde. This is the usual method of use, i.e., as a monomer. Solutions can also be made as paraformaldehyde is somewhat soluble in hot water.

Trioxane. Some amounts of formaldehyde are made from trioxane, a cyclic trimer of formaldehyde:

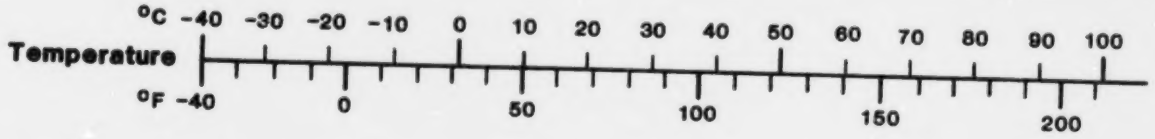


This colourless, crystalline solid has a melting point of 61-62°C, a boiling point of 115°C, and a solubility in water of 21 g/100 mL (25°C). At 25°C, the vapour pressure is 1.7 kPa; the viscosity of the melt at 65°C is 2 mPa·s. Trioxane can be depolymerized to formaldehyde under acid conditions such as over phosphoric acid on silicon carbide at 150-200°C.

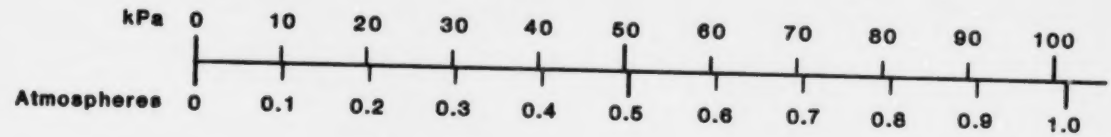
TABLE 1

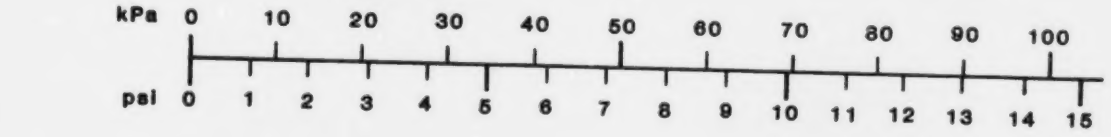
FORMALDEHYDE

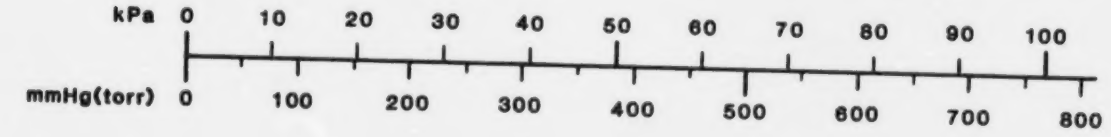
CONVERSION NOMOGRAMS



Pressure 1 kPa = 1 000 Pa







Viscosity

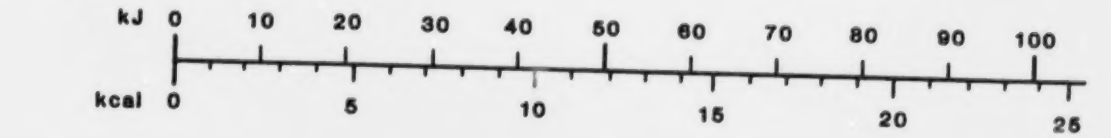
Dynamic 1 Pa·s = 1 000 centipoise (cP)

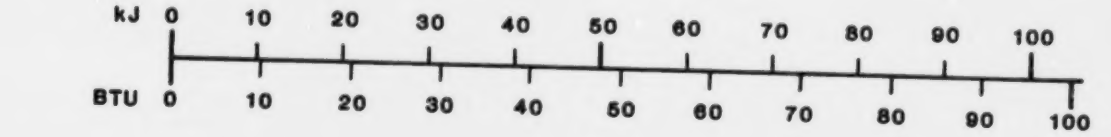
Kinematic 1 m^2/s = 1 000 000 centistokes (cSt)

Concentration (in water)

1 ppm ≅ 1 mg/L

Energy (heat) 1 kJ = 1 000 J





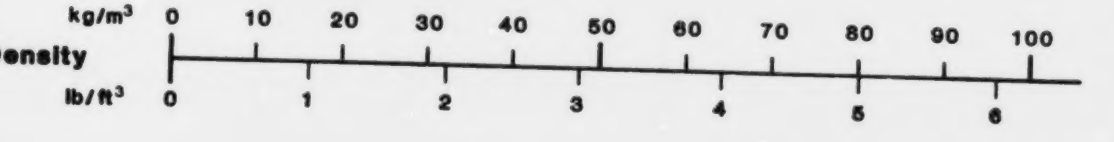


FIGURE 1

FORMALDEHYDE

VAPOUR PRESSURE

Reference: ULLMANN 1975; PPH 1974

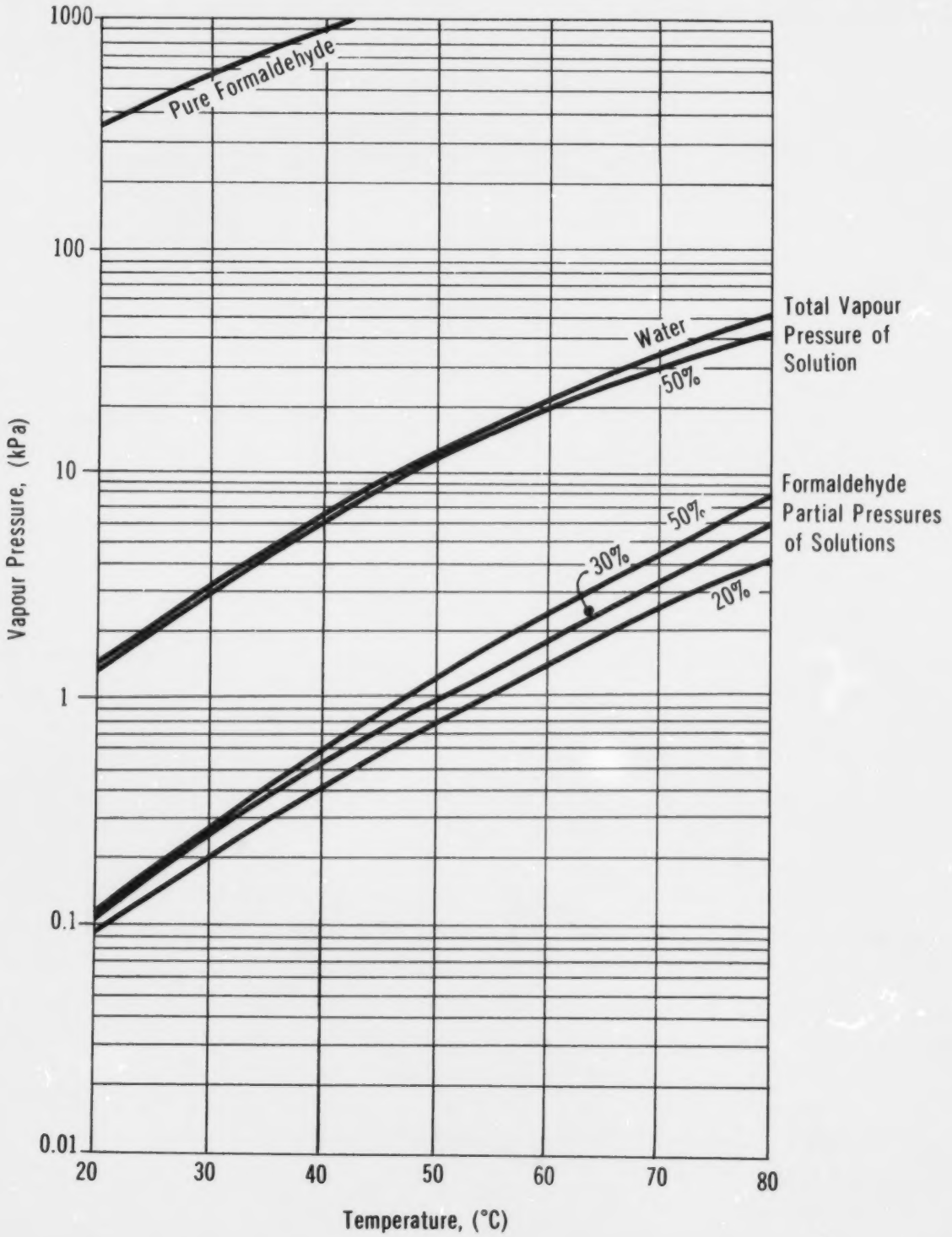
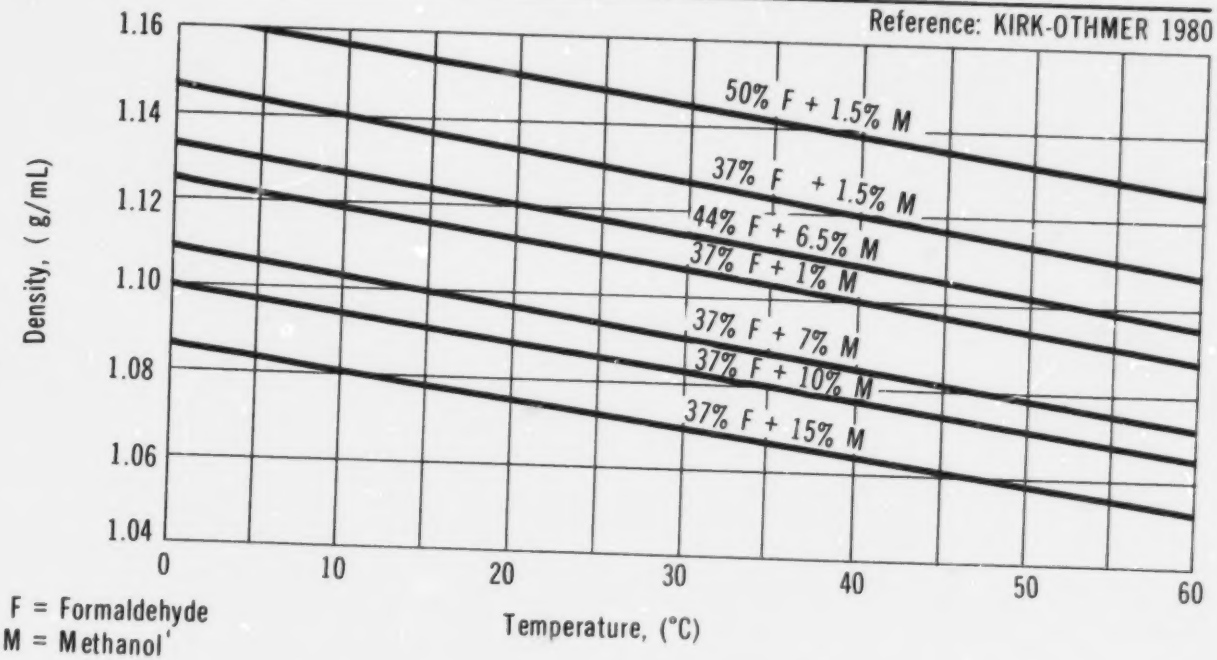


FIGURE 2

FORMALDEHYDE (Solutions)

LIQUID DENSITY

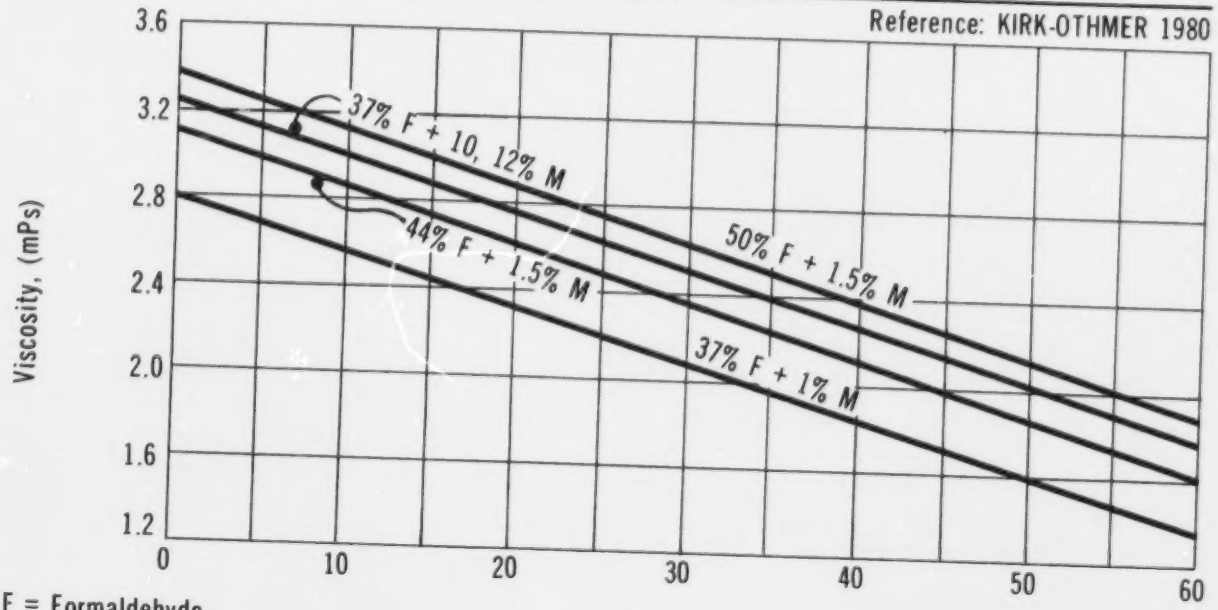


F = Formaldehyde
M = Methanol

FIGURE 3

FORMALDEHYDE (Solutions)

LIQUID VISCOSITY



F = Formaldehyde
M = Methanol

FIGURE 4

FORMALDEHYDE (Solutions)

MINIMUM STORAGE TEMPERATURE

Reference: KIRK-OTHMER 1980

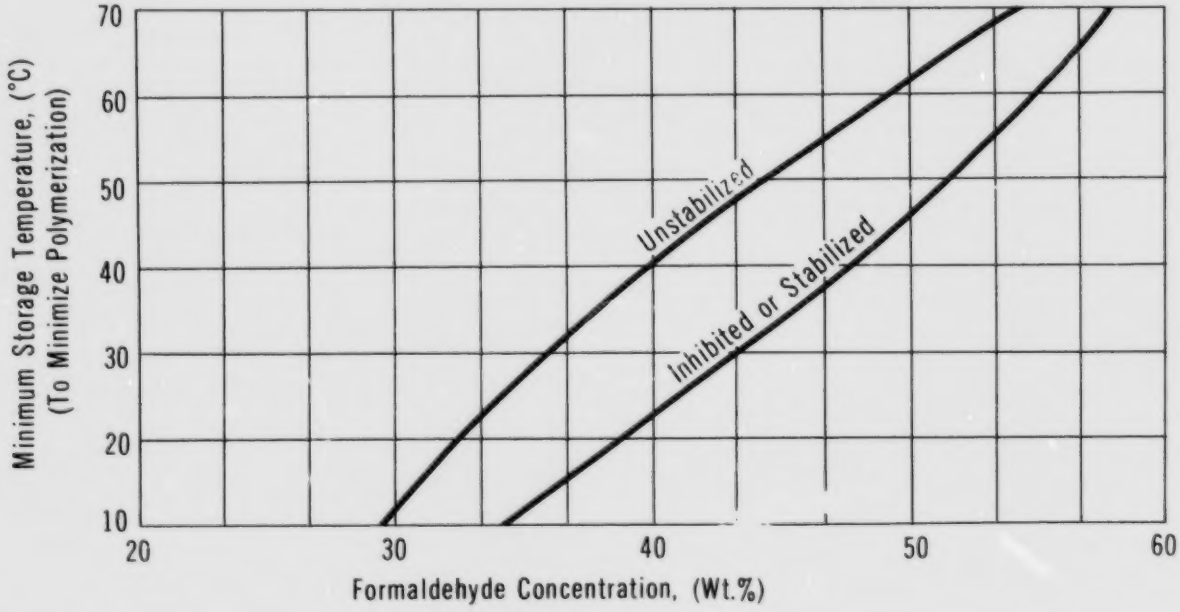
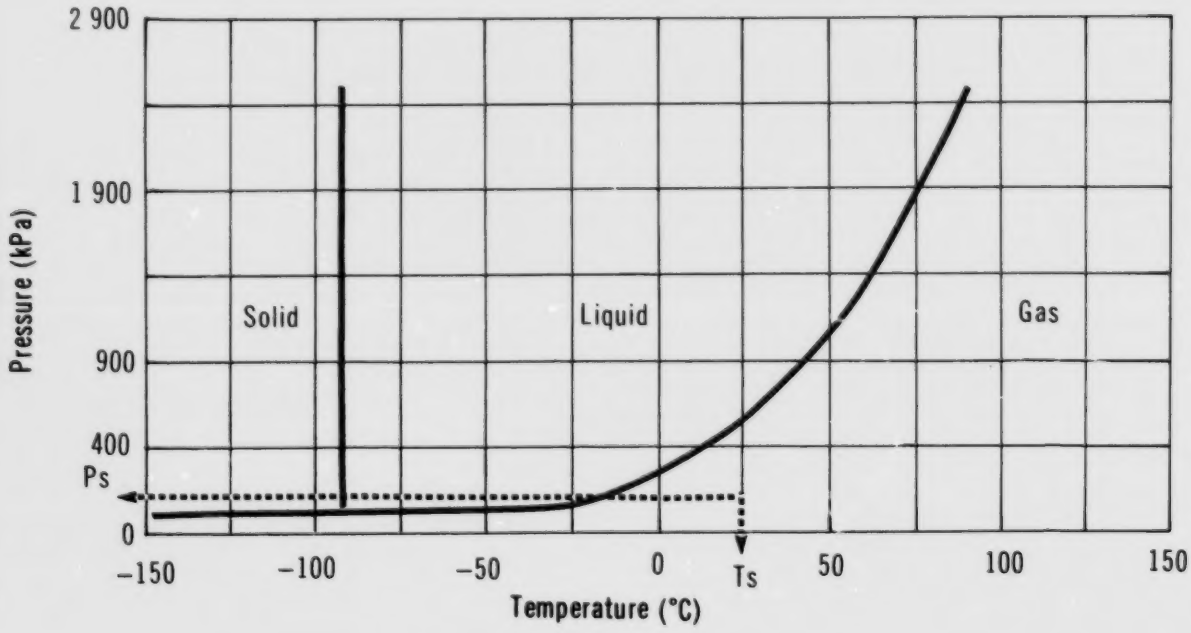


FIGURE 5

FORMALDEHYDE

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities (Celanese MSDS 1979; Celanese PB; Corpus 1984; Kirk-Othmer 1980)

Formaldehyde is sold in concentrations from 37 to 52 percent by weight. In Canada, as elsewhere, formaldehyde is mainly produced and available as 37 percent formalin solution, inhibited with methyl alcohol. The following is a table of commonly available solutions:

	Weight Percent								
Formaldehyde	37	37	37	37	44	44	45	50	52
Methanol	1	6.5-7.5	10	12-15	1-2	6-7	1-1.5	1-1.5	1-1.5
Acidity as formic acid (max)	0.03	0.03	0.03	0.03	0.04	0.04	0.04	0.05	0.04
Notes	uninhibited				uninhibited		uninhibited		

Paraformaldehyde is sold as a flake with a purity of 91 percent or as a powder with a purity of 95 percent. The remainder is mostly water. Trioxane is typically sold in purities of 99 percent and greater in flake or block forms.

3.2 Domestic Manufacturers (Corpus 1984; CCPA 1981; Scott 1979)

These are corporate headquarters' addresses and are not intended as spill response contacts:

Bakelite Thermosets
20 Eglinton Avenue West, Suite 1107
Toronto, Ontario
M4R 1K8
(416) 487-5521

The Borden Co. Ltd.
Borden Chemical Division
1275 Lawrence Avenue East
Don Mills, Ontario
M3A 1C5
(416) 445-3131

Celanese Canada Inc.
800 Dorchester Blvd. West
Montreal, Quebec
H3C 3K8
(514) 878-1581

Reichhold Ltd.
600 The East Mall
Islington, Ontario
M9B 4B1
(416) 622-5540

3.3 Other Suppliers (Corpus 1984; CBG 1980; Scott 1979)

A & K Petro-Chem Industries Ltd.
710 Arrow Road
Weston, Ontario
M9M 2M1
(416) 746-2991

Arliss Chemical Co. Inc.
325 Hymus Blvd.
Pointe-Claire, Quebec
H9R 1G8
(514) 694-2170

Benson Chemicals Ltd.
P.O. Box 10
Freelton, Ontario
L0R 1K0
(416) 659-3351

Canada Colours & Chemicals Ltd.
80 Scarsdale Road
Don Mills, Ontario
M3B 2R7
(416) 924-6831

Degussa (Canada) Ltd.
3370 South Service Road
Burlington, Ontario
L7N 3M6

Du Pont Canada Inc.
555 Dorchester Blvd. West
Montreal, Quebec
H3C 2V8
(514) 861-3861

Harrisons & Crosfield (Canada) Ltd.
4 Banigan Drive
Toronto, Ontario
M4H 1G1
(416) 425-6500

Lawrason's Chemical Ltd.
180 Adelaide Street South
Box 2425
London, Ontario
N6A 4G3
(519) 686-9335

Mailloux Chemical & Dyestuff Ltd.
875 Selkirk Street
Pointe-Claire, Quebec
H9R 3S2
(514) 695-8702

Mallinckrodt Canada Inc.
600 Delmar Avenue
Pointe-Claire, Quebec
H9W 1E6
(514) 695-1220

Shefford Chemicals Ltd.
1028 Principale
Granby, Quebec
J2G 8C8
(514) 378-0125

Stanchem Div. PPG Ind. Canada Ltd.
5029 St. Ambroise Street
Montreal, Quebec
H4C 2E9

Winfield Chemical Industries Ltd.
P.O. Box 1134
Woodstock, New Brunswick
E0J 2B0
(506) 328-6851

3.4 Major Transportation Routes

Current Canadian production of formaldehyde is located in Quebec, Ontario, Alberta, and British Columbia. Formaldehyde solution is shipped universally across Canada.

3.5 Production Levels (Corpus 1984)

Company, Plant Location		Nameplate Capacity kilotonnes/yr (1983)
Bakelite Thermosets, Belleville, Ont.		19
Borden Chemical, Laval, Que.		8.5
Borden Chemical, Toronto, Ont.		6.5
Borden Chemical, North Bay, Ont.		4.5
Borden Chemical, Edmonton, Alta.		10
Borden Chemical, West Vancouver, B.C.		10
Celanese Canada, Edmonton, Alta.		50
Reichhold, Ste. Therese Que.		7.5
Reichhold, North Bay, Ont.		31.5
Reichhold, Port Moody, B.C.		8.5
Reichhold, Thunder Bay, Ont.		20
	TOTAL	176
Domestic Production (1983)		116
Imports (1983)		3.2
	TOTAL SUPPLY	119.2

3.6 Manufacture of Formaldehyde (Walker 1964; Kirk-Othmer 1980)

3.6.1 General. Formaldehyde is generally produced by catalytic air oxidation of methanol.

3.6.2 Manufacturing Process. Metered quantities of methanol vapour and air are mixed in a mixing chamber. From this chamber, the mixture is piped to a catalyst-bed converter, where the reaction

$$CH_3OH + 1/2\ O_2 \rightarrow CH_2O + H_2O$$

takes place. Depending on the catalyst system used (metal oxides or metallic systems), the reaction occurs at 300-650°C and atmospheric pressure. The product is cooled and (depending on process details) piped to a methanol-formaldehyde separation unit or to an absorption column to produce 37 percent formaldehyde solution. Finally, formic acid is removed by ion exchange.

3.6.3 Byproducts. Carbon monoxide, dimethyl ether, carbon dioxide, formic acid and methyl formate are byproducts of the reaction.

3.7 **Major Uses in Canada** (Corpus 1984; CCP 1981)

Formaldehyde is used in the manufacture of phenolic resins, urea resins, melamine and resorcinol resins, pentaerythritol, fatty amides, hexamine, disinfectants, germicides and embalming fluids as a preservative, and in precious metal recovery. In 1983, 35 percent of domestic production was used for urea resin production, 31 percent for phenolic resin production, and 24 percent for pentaerythritol production.

3.8 **Major Buyers in Canada** (Corpus 1984; CBG 1980)

Alkanil Chemicals, Mississauga, Ont.
Almatex, London, Ont.
Bakelite Thermosets, Belleville, Ont.
Benson Chemicals, Freelton, Ont.
Canada Colors and Chemicals, Toronto, Ont.
Canadian Occidental, Fort Erie, Ont.
Canadian General Electric, Toronto, Ont.
C-I-L, Courtwright, Ont.
C-I-L, Paints, Toronto, Ont.
Cominco, Carseland, Alta.
Cyanamid Canada, St. Jean, Que.
Diamond Shamrock, Hamilton, Ont.
Domtar, Concord, Ont.; LaSalle, Que.
Domtex, Montreal, Que.
Fiberglas Canada, Sarnia, Ont.
GBS - Gioca, Niagara Falls, Ont.
Glidden (SCM), Toronto, Ont.
Goodyear Canada, Toronto, Ont.
Harrisons & Crosfield, Toronto, Ont.
Inmont Canada, Toronto, Ont.
Lawrason's Chemicals, London, Ont.
Lawrer Chemicals (Canada), Toronto, Ont.
Mailloux Chemicals, Montreal, Que.
Monsanto Canada, LaSalle, Que.
Moore Benjamin, Toronto, Ont.
PPG Industries Canada, Toronto, Ont.
Reichhold, Port Moody, B.C.
Schenectady Chemicals, Toronto, Ont.
Shefford Chemicals, Granby, Que.
Simplot Chemical, Brandon, Man.
Stanchem Distribution, Montreal, Que.
Sterling Varnish, St. Catharines, Ont.
Uniroyal Chemicals, Elmira, Ont.
Winfield Chemical Industries, Woodstock, N.B.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 Bulk Shipment. Transportation vessels and containers under this category have been grouped under the classifications of railway tank cars and highway tank vehicles. Formaldehyde is only shipped bulk as an aqueous solution (MCA 1960).

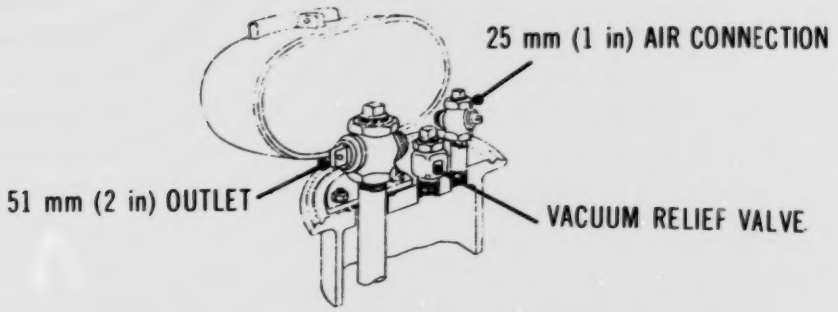
4.1.1.1 Railway tank cars. Railway tank cars used to transport formaldehyde are described in Table 2 (TCM 1979; RTDCR 1974). Figure 6 shows a typical railway car used to transport formaldehyde; Table 3 indicates railway tank car specifications associated with this drawing. For formaldehyde service, cars may be lined or even constructed of stainless steel. Cars are equipped for unloading by pump or gravity flow through a 152 mm (6 in.) diameter bottom outlet (TDGC 1980). Unloading the cars through the connection at the top of the car by pump is the preferred method of unloading. In this case, the liquid is withdrawn through an eduction pipe which extends from the bottom of the tank to the top operating platform where it terminates with an unloading connection valve. Air pressure is not used for unloading formaldehyde tanks (MCA 1960).

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS

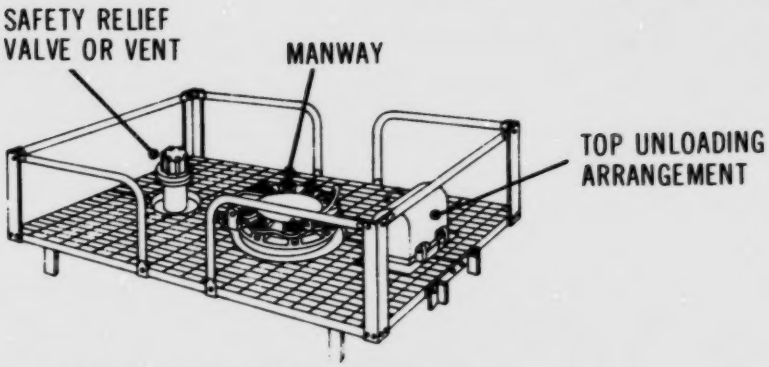
CTC/DOT* Specification Number	Description
111A60W1	Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Test pressure 414 kPa (60 psi).
111A60F1	Steel forge-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Test pressure 414 kPa (60 psi).
111A100W1	Steel fusion-welded tank without dome. Uninsulated or insulated. 2% minimum outage. Gauging device. Bottom outlet or washout optional. Test pressure 690 kPa (100 psi).
111A60W1 (1L)	Same as 111A60W1 only interior lined.

* Canadian Transport Commission and Department of Transportation (U.S.)

(Reference - TCM 1979, RTDCR 1974)



Detail of top unloading arrangement



Detail of loading platform

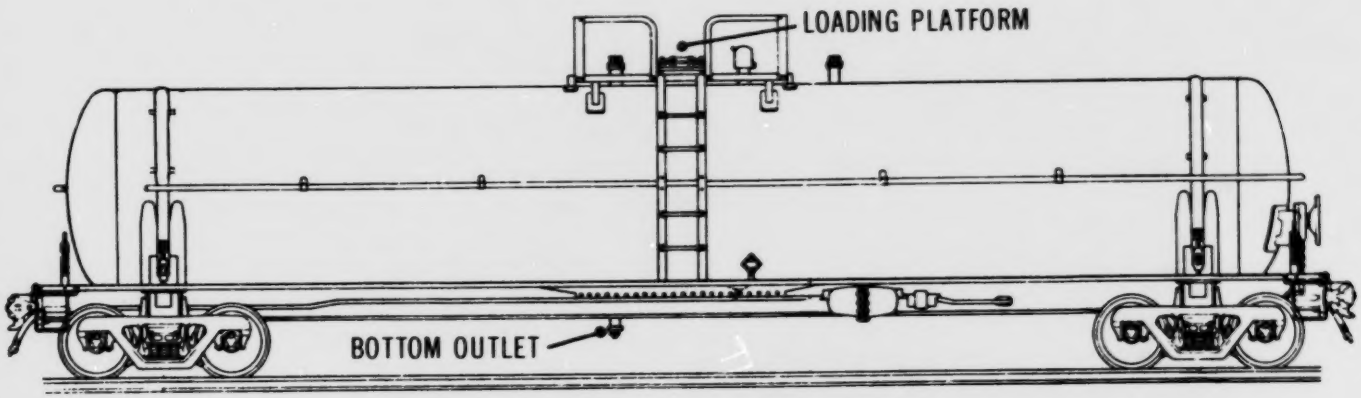


Illustration of tank car layout

TABLE 3 TYPICAL RAILWAY TANK CAR SPECIFICATIONS - CLASS 111A60W1 (TCM 1979; RTDCR 1974)

Description	Tank Car Size (Imp. Gal.)					
	16 700		17 200		20 000	
Overall						
Nominal capacity	75 700 L	(16 700 gal.)	78 000 L	(17 200 gal.)	90 900 L	(20 000 gal.)
Car weight - empty	33 900 kg	(74 700 lb.)	33 900 kg	(74 700 lb.)	38 900 kg	(85 800 lb.)
Car weight - max.	119 000 kg	(263 000 lb.)	83 500 kg	(184 000 lb.)	119 000 kg	(263 000 lb.)
Tank						
Material	Steel		Steel		Steel	
Thickness	11.1 mm	(7/16 in.)	11.1 mm	(7/16 in.)	11.1 mm	(7/16 in.)
Inside diameter	2.60 m	(102 in.)	2.62 m	(103 in.)	2.74	(108 in.)
Test pressure	414 kPa	(60 psi)	414 kPa	(60 psi)	414 kPa	(60 psi)
Burst pressure	1640 kPa	(240 psi)	1640 kPa	(240 psi)	1640 kPa	(240 psi)
Approximate Dimensions						
Coupled length	17 m	(57 ft.)	17 m	(57 ft.)	18 m	(60 ft.)
Length over strikers	16 m	(53 ft.)	16 m	(53 ft.)	17 m	(57 ft.)
Length of truck centres	13 m	(42 ft.)	13 m	(42 ft.)	14 m	(45 ft.)
Height to top of grating	4 m	(12 ft.)	4 m	(12 ft.)	4 m	(13 ft.)
Overall height	5 m	(15 ft.)	5 m	(15 ft.)	5 m	(15 ft.)
Overall width (over grabs)	3.2 m	(127 in.)	3.2 m	(127 in.)	3.2 m	(127 in.)
Length of grating	2 to 3 m	(8 to 10 ft.)	2 to 3 m	(8 to 10 ft.)	2 to 3 m	(8 to 10 ft.)
Width of grating	1.5 to 2 m	(5 to 6 ft.)	1.5 to 2 m	(5 to 6 ft.)	1.5 to 2 m	(5 to 6 ft.)
Loading/Unloading Fixtures						
Top Unloading						
Unloading connection	51 mm	(2 in.)	51 mm	(2 in.)	51 mm	(2 in.)
Manway/fill hole	203 to 356 mm	(8 to 14 in.)	203 to 356 mm	(8 to 14 in.)	203 to 356 mm	(8 to 14 in.)
Air connection	25 to 51 mm	(1 to 2 in.)	25 to 51 mm	(1 to 2 in.)	25 to 51 mm	(1 to 2 in.)
Bottom Unloading						
Bottom outlet	102 to 152 mm	(4 to 6 in.)	102 to 152 mm	(4 to 6 in.)	102 to 152 mm	(4 to 6 in.)
Safety Devices	Safety vent or valve					
Dome	None					
Insulation	Optional					

A safety relief valve set at 241 kPa (35 psi) or a safety vent set at 414 kPa (60 psi) is required on top of the rail car (TCM 1979). A gauging device, either the rod type or the tape type, is required. The top unloading connection must be protected by a housing. The maximum pressure allowable for the CTC/DOT 111A100W1 rail cars is 448 kPa (65 psi). When the 111A60W1 or 111A60F1 cars are used, the maximum pressure would be 276 kPa (40 psi) (TCM 1979).

4.1.1.2 Tank motor vehicles. Formaldehyde is transported by tank motor vehicles with tanks classed as nonpressure vessels. Design pressure for such tanks does not exceed 14 kPa (2 psi). Motor vehicle tanks are similar to the railway tanks previously described. These highway tankers are usually unloaded by pump from the top unloading connection valve. Air pressure should not be used (MCA 1960). The off-loading equipment and procedures for tank motor vehicles are similar to those for railway tank cars, to be discussed later.

4.1.2 Packaging. Formaldehyde, in addition to railway bulk shipments, is also transported in drums, carboys, barrels and bottles. Drums fabricated from a variety of construction materials are permitted, as described in Table 4 (TDGC 1980). Paraformaldehyde is usually shipped in bags, lined fibre drums, and boxes. Trioxane is available in lined fibre drums or as a block (25 kg) (50 lb.) in polyethylene-lined cartons.

4.2 Off-loading

4.2.1 Off-loading Equipment and Procedures for Railway Tank Cars. Prior to off-loading, certain precautions must be taken (MCA 1960):

- The storage tank must be checked to make sure that it will hold the contents of the car.
- For night-time unloading, lights must have an explosion-proof rating.
- Personnel must not enter the car under any circumstances.
- Brakes must be set, wheels chocked, derails placed and caution signs displayed.
- A safe operating platform must be provided at the unloading point.
- Tools used during unloading must be spark-resistant.
- Effectively ground the tank car.

Two means of off-loading are used for rail cars, top off-loading and bottom off-loading.

TABLE 4 DRUMS

Type of Drum	Designation	Description
Steel (may be lined for formaldehyde service)	1A1	Nonremovable head, reusable
	1A1A	1A1 with reinforced chime
	1A1B	1A1 with welded closure flange
	1A1D	1A1 with coating (other than lead)
	1A2	Removable head, reusable
	1A3	Nonremovable head, single use only
Monel*	TC5M	
Aluminum	1B1	Nonremovable head
	1B2	Removable head
Steel Drums with inner plastic receptacles	6HA1	Outer steel sheet in the shape of drum. Inner plastic receptacle. Maximum capacity of 225 L (49 gal.)
Fibreboard Drums with inner plastic receptacles	6HG1	Outer containers of convolutely wound plies of fibreboard. Inner plastic in shape of drum. Maximum capacity of 225 L (49 gal.)

*See Section 4.3 of this report.

Proceed with top off-loading as follows (MCA 1960):

- In cold weather, precautions are taken to keep temperatures above the minimum specified.
- After removing the protective housing from the discharge line at the top of the car, connect the 51 mm (2 in.) unloading line.
- Off-load the tanker by pump only.

Proceed with bottom off-loading in the following manner using gravity flow or pump:

- After connecting the unloading line to a 152 mm (6 in.) bottom outlet, open the inside bottom valve by turning the valve rod handle at the top of the car.
- Off-load the car by gravity or pump.

4.2.2 Specifications and Materials for Off-loading Equipment. The materials of construction for off-loading system components discussed in this section along with specifications refer to those generally used. It is recognized that other materials may be used for particular applications, as indicated in Table 5. The components of a typical off-loading system that will be discussed include pipes and fittings, flexible connections, valves, gaskets and pumps.

Schedule 40 seamless steel pipes and fittings lined with chlorinated polyether resins are recommended for formaldehyde lines (DCRG 1978). Flanged joints should be used and these should be welded, because threaded pipes and fittings tend to leak after a very short time. Stress relief at the weld will also lengthen the serviceability of the pipe.

The unloading line should be 52 mm (2 in.) pipe because this is the standard fitting on tank cars; process pipe may be almost any size. Pipe under 25 mm (1 in.), however, is not recommended. Outdoor lines must be self-draining.

Flexible bellows-type expansion joints should be used for the flexible sections of the unloading line. They are manufactured with ASA ductile iron flanges with expansion members molded from tetrafluoroethylene resin (Dow PPS 1972). Aluminum, stainless steel or flexhose lines may be used for unloading (Law 1982).

Cast iron or cast steel diaphragm valves lined with chlorinated polyether or polyvinylidene chloride resin will serve adequately (Dow PPS 1972). Only Viton should be used as a gasket material at normal temperature ranges (DCRG 1978).

A single-suction, positive displacement pump with "wet end" material of 316 stainless steel gives good results (HIS 1969). Provision must be made for draining the pump so that repairs can be made safely. The pump should be equipped with flanges at both suction and discharge openings; screw connections are more subject to leakage and should be avoided.

Storage tanks fabricated of stainless steel or lined carbon steel should be temperature-controlled because polymer precipitation takes place at low temperatures and hazardous vapours may be given off at high temperatures (MCA 1960).

4.3 Compatibility with Materials of Construction

The compatibility of formaldehyde with materials of construction is indicated in Table 5. The unbracketed abbreviations are described in Table 6. The rating system for this report is briefly described below.

Recommended: This material will perform satisfactorily in the given application.

Conditional: Material will show deterioration in the given application; however, it may be suitable for intermittent or short-term service.

Not Recommended: Material will be severely affected in this application and should not be used.

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings	37%	52	PVDC PVDF (DCRG 1978)		
		66			SS 304 (Celanese PD)
		93	PP (DCRG 1978)		
		107	Chlorinated Polyether (DCRG 1978)		
		All	SS 316 (Celanese PD)		
	50%	52	PVDC (DCRG 1978)		
		93	PP (DCRG 1978)		
		107	Chlorinated Polyether (DCRG 1978)		
	Most	23	PVC I (DPPED 1967)	PVC II (DPPED 1967)	
		60		PVC I (DPPED 1967)	PVC II (DPPED 1967)
		24	PE (MWPP 1978)		
		To operating limit of material	PVC I* ABS (MWPP 1978) SS (MCA 1960)		

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
2. Valves	All	Cold and boiling	Alloy 20 SS 316 (JSSV 1979)		
3. Pumps	All	49	GRP with FPM "0" ring		
			All bronze SS 304 SS 316 (HIS 1969)		
4. Storage	Most	< 50	SS CS lined Aluminum (MCA 1960)	CS Copper (MCA 1960)	
	All	<66	SS 304, SS 316, SS 347, CS lined (Kirk-Othmer 1980)		
		>66			SS 304 (Celanese PD)
5. Others	37%	21	PVDF (TPS 1978)		
		22	CPVC (TPS 1978)		
		60	PVC (TPS 1978)		
		66		PP (TPS 1978)	
		85			CPVC (TPS 1978)
	40%	60	uPVC, PE PP, POM NR*, NBR* IIR, EPDM* CR*, FPM CSM* (GF)		
		Boiling	SS 302 SS 304 SS 316 SS 430 (ASS)	SS 410 (ASS)	

TABLE 5 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
5. Others (Cont'd)	20	SBR		NR	
			IIR CSM EPDM (GPP)		CR NBR (GPP)
		70			NR SBR CR CSM EPDM (GPP)
	10 to 70, 100%	24 to 100	Glass (CDS 1967)		
	80%	24	Glass (CDS 1967)		
	10 to 30, 100%	24			Concrete (CDS 1967)
	20%	24 to 52	Wood (CDS 1967)		
	100%	24		Wood (CDS 1967)	

*This material has been given a lower rating in a similar application by another reference.

TABLE 6 MATERIALS OF CONSTRUCTION

Abbreviation	Material of Construction
ABS	Acrylonitrile Butadiene Styrene
	Alloy 20
	Aluminum
	Bronze
	Chlorinated Polyether
CPVC	Chlorinated Polyvinyl Chloride

TABLE 6 MATERIALS OF CONSTRUCTION (Cont'd)

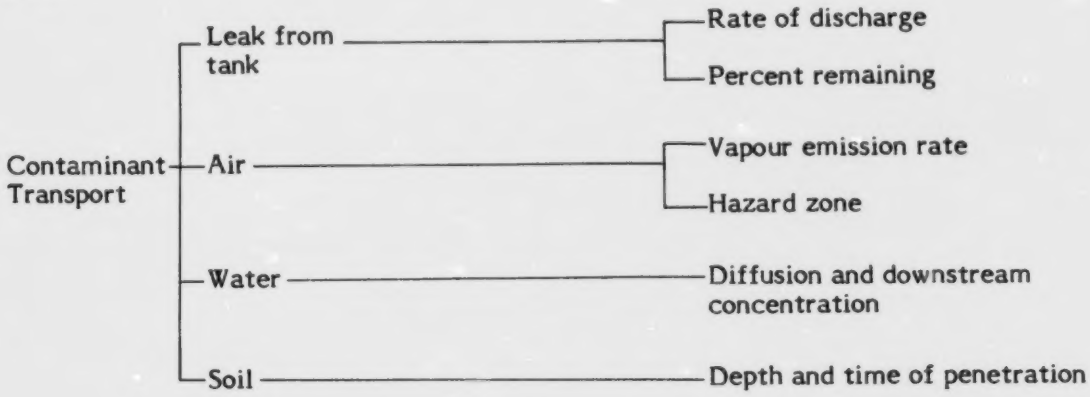
Abbreviation	Material of Construction
CR	Polychloroprene (Neoprene)
CS	Carbon Steel
CSM	Chlorosulphonated Polyethylene (Hypalon)
	Concrete
	Copper
EPDM	Ethylene Propylene Rubber
FPM	Fluorine Rubber (Viton)
	Glass
GRP	Glass Reinforced Vinyl Ester
IIR	Isobutylene/Isoprene (Butyl) Rubber
NBR	Acrylonitrile/Butadiene (Nitrile, Buna N) Rubber
NR	Natural Rubber
	Nickel-Copper Alloy (Monel)
PE	Polyethylene
POM	Polyoxymethylene
PP	Polypropylene
PVC (Followed by grade, if any)	Polyvinyl Chloride
PVDC	Polyvinylidene Chloride
PVDF	Polyvinylidene Fluoride
SBR	Styrene/Butadiene (GR-5, Buna S) Rubber
SS (Followed by grade)	Stainless Steel
uPVC	Unplasticized Polyvinyl Chloride
	Wood

5 CONTAMINANT TRANSPORT

5.1 General Summary

Formaldehyde is commonly transported in 30 to 52 percent aqueous solution in railway tank cars and tank trucks. When spilled in water, formaldehyde solution will mix. When spilled on soil, the liquid will spread on the surface and penetrate into the soil at a rate dependent on the soil type and its water content. Downward transport of the liquid toward the groundwater table may be an environmental concern. Vapour from a spill will be released continuously to the atmosphere by evaporation.

The following factors are considered for the transport of a spill in water and soil:



It is important to note that, because of the approximate nature of the contaminant transport calculations, the approach adopted throughout has been to use conservative estimates of critical parameters so that predictions are approaching worst case scenarios for each medium. This may require that the assumptions made for each medium be quite different and to some extent inconsistent. As well as producing worst case scenarios, this approach allows comparison of the behaviours of different chemicals under the same assumptions.

5.2 Leak Nomograms

5.2.1 Introduction. Formaldehyde solution is commonly transported in railway tank cars and tank trucks as a nonpressurized liquid. While the capacities of the tank cars vary widely, one tank car size has been chosen throughout the EnviroTIPS series for development of the leak nomograms. It is approximately 2.75 m in diameter and 13.4 m long, with a carrying capacity of about 80 000 L.

If a tank car loaded with formaldehyde solution is punctured on the bottom, all of the contents will drain out by gravity. The aim of the nomograms is to provide a simple means to obtain the time history of the conditions in the tank car and the venting rate of the liquid. Because of the relatively low volatility of formaldehyde solutions and the fact that the tank cars are not pressurized, no leak nomograms have been prepared for vapour release from a puncture in the top of the tank.

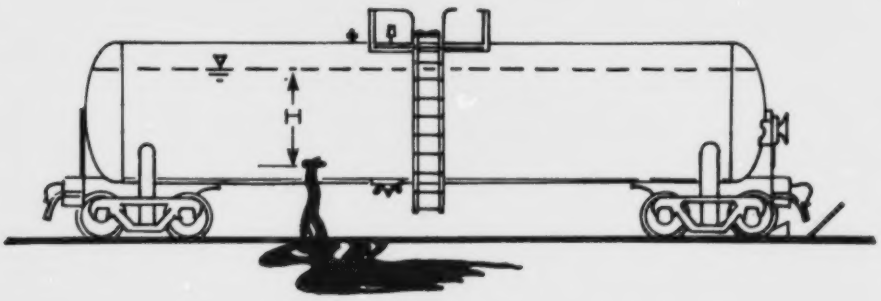


FIGURE 7 TANK CAR WITH PUNCTURE HOLE IN BOTTOM

The rate of outflow (q) from a vent hole in the bottom of the tank car is defined by the standard orifice equation (Streeter 1971). It is a function of the hole size (A) and shape, the height of the liquid above the puncture hole (H), and a coefficient of discharge (Cd).

As the gravitational force predominates over viscous and other forces for a wide range of fluid conditions, the rate of discharge is relatively independent of fluid temperature and viscosity (Rouse 1961). Consequently, it is reasonable to assume a constant discharge coefficient for formaldehyde solution for a wide range of temperature and viscosity. For the purposes of nomogram preparation, a constant discharge coefficient of 0.8 has been assumed.

5.2.2 Nomograms.

5.2.2.1 Figure 8: Percent remaining versus time. Figure 8 provides a means of estimating the percent of liquid remaining in the standard tank car after the time of puncture for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

FIGURE 8

FORMALDEHYDE (37% SOLUTION)

PERCENT REMAINING VS TIME

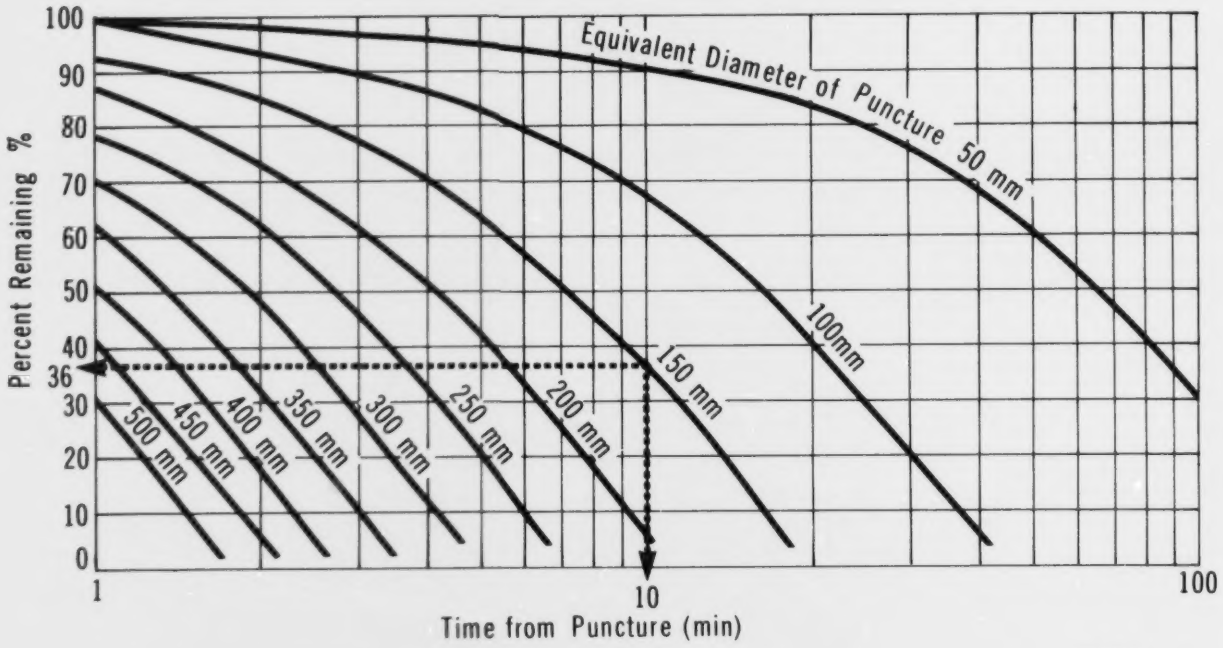
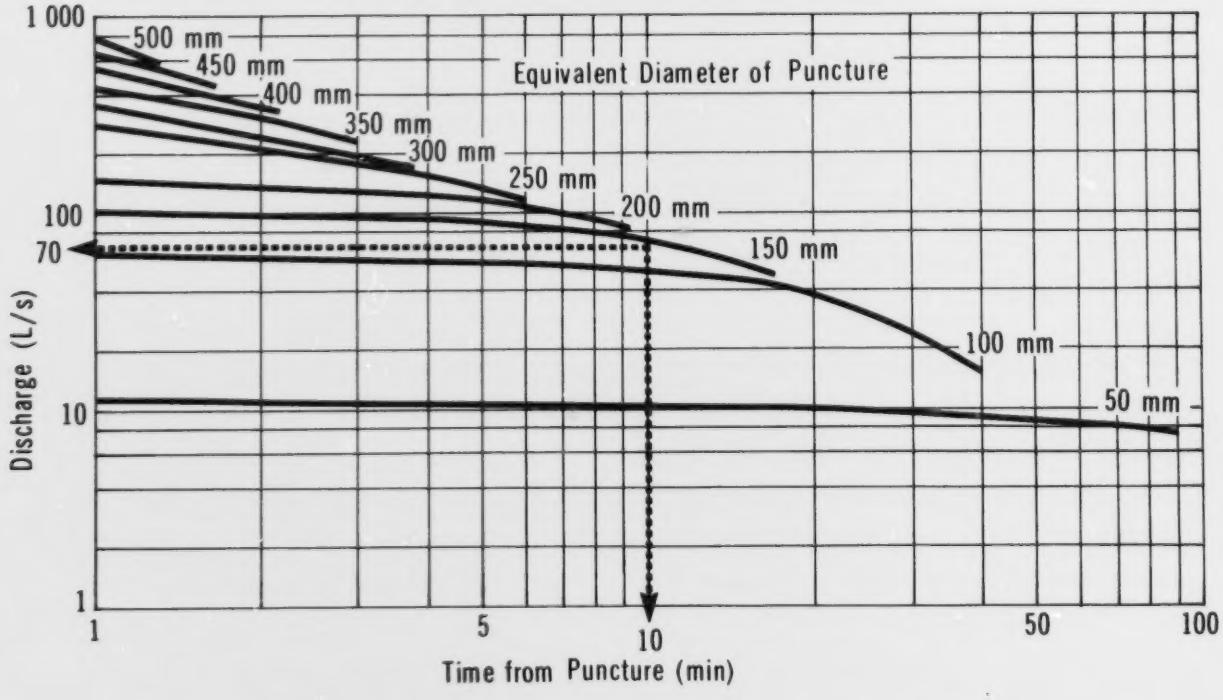


FIGURE 9

FORMALDEHYDE (37% SOLUTION)

DISCHARGE RATE VS TIME



The standard tank car is assumed to be initially full (at t=0) with a volume of about 80 000 L of formaldehyde solution. The amount remaining at any time (t) is not only a function of the discharge rate over time, but also of the size and shape of the tank car.

5.2.2.2 Figure 9: Discharge rate versus time. Figure 9 provides a means of estimating the instantaneous discharge rate (L/s) at any time (t) after the time of puncture for a number of equivalent hole diameters. The nomogram is only applicable to the standard tank car size with an initial volume of 80 000 L.

5.2.3 Sample Calculations.

i) Problem A

The standard tank car filled with formaldehyde solution has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the initial 80 000 L remains after 10 minutes?

Solution to Problem A

- Use Figure 8
- With t=10 min and d=150 mm, the amount remaining is about 36 percent or 28 800 L

ii) Problem B

With the same conditions as Problem A, what is the instantaneous discharge rate from the tank 10 minutes after the accident?

Solution to Problem B

- Use Figure 9
- With t=10 min and d=150 mm, the instantaneous discharge rate (q) =70 L/s

5.3 Dispersion in the Air

5.3.1 Introduction. Since formaldehyde solutions are relatively nonvolatile, direct venting of the vapour to the atmosphere from a hole in a punctured vessel does not constitute a significant hazard downwind. Only vapour released from a liquid pool spilled on a ground or water surface is treated here.

To estimate the vapour concentrations downwind of the accident site for the determination of the flammability or toxicity hazard zone, the atmospheric transport and dispersion of the contaminant vapour must be modelled. The models used here are based

on Gaussian formulations and are the ones most widely used in practice for contaminant concentration predictions. The model details are contained in the Introduction Manual.

Figure 10 depicts schematically the contaminant plume configuration from a continuous surface release. The dispersion model represents the liquid pool area source as a virtual point source (with the same vapour emission rate, Q) located 10 equivalent pool radii upwind.

5.3.2 Vapour Dispersion Nomograms and Tables. The aim of the air dispersion nomograms is to define the hazard zone due to toxicity or flammability of a vapour cloud. The following nomograms and data tables are contained in this section (to be used in the order given):

Figure 12:	vapour emission rate from a liquid pool as a function of maximum pool radius
Table 7:	weather conditions
Figure 13:	normalized vapour concentration as a function of downwind distance and weather conditions
Table 8:	maximum plume hazard half-widths
Figure 16:	vapour plume travel distance as a function of time elapsed since the spill and wind speed

The flowchart given in Figure 11 outlines the steps necessary to make vapour dispersion calculations and identifies the nomograms or tables to be used. This section deals only with the portion contained within the dashed box. Data on "total liquid discharged" is contained in Section 5.2. A description of each vapour dispersion nomogram and its use follows.

5.3.2.1 Figure 12: Vapour emission rate versus liquid pool radius for various temperatures. An evaporation rate for a 37 percent formalin solution has been calculated employing the evaporation rate equations contained in the Introduction Manual. The computed evaporation rate for the 37 percent solution at 20°C and a wind speed of 4.5 m/s (16.1 km/h) is 0.015 g/(m^2s). Evaporation rates at other temperatures have been calculated using the evaporation rate equation which at a given wind speed is dependent on ambient temperature and the vapour pressure (CHRIS 1978) of the solution at that temperature. For example, evaporation rates of 3.6×10^{-3} g/(m^2s) at 0°C and 0.021 g/(m^2s) at 30°C were calculated for a wind speed of 4.5 m/s. Note that in an actual spill situation, formaldehyde vapour released from the liquid pool will lower the concentration of formaldehyde in the liquid phase and result in lower formaldehyde

FIGURE 10

FORMALDEHYDE

SCHEMATIC OF CONTAMINANT PLUME

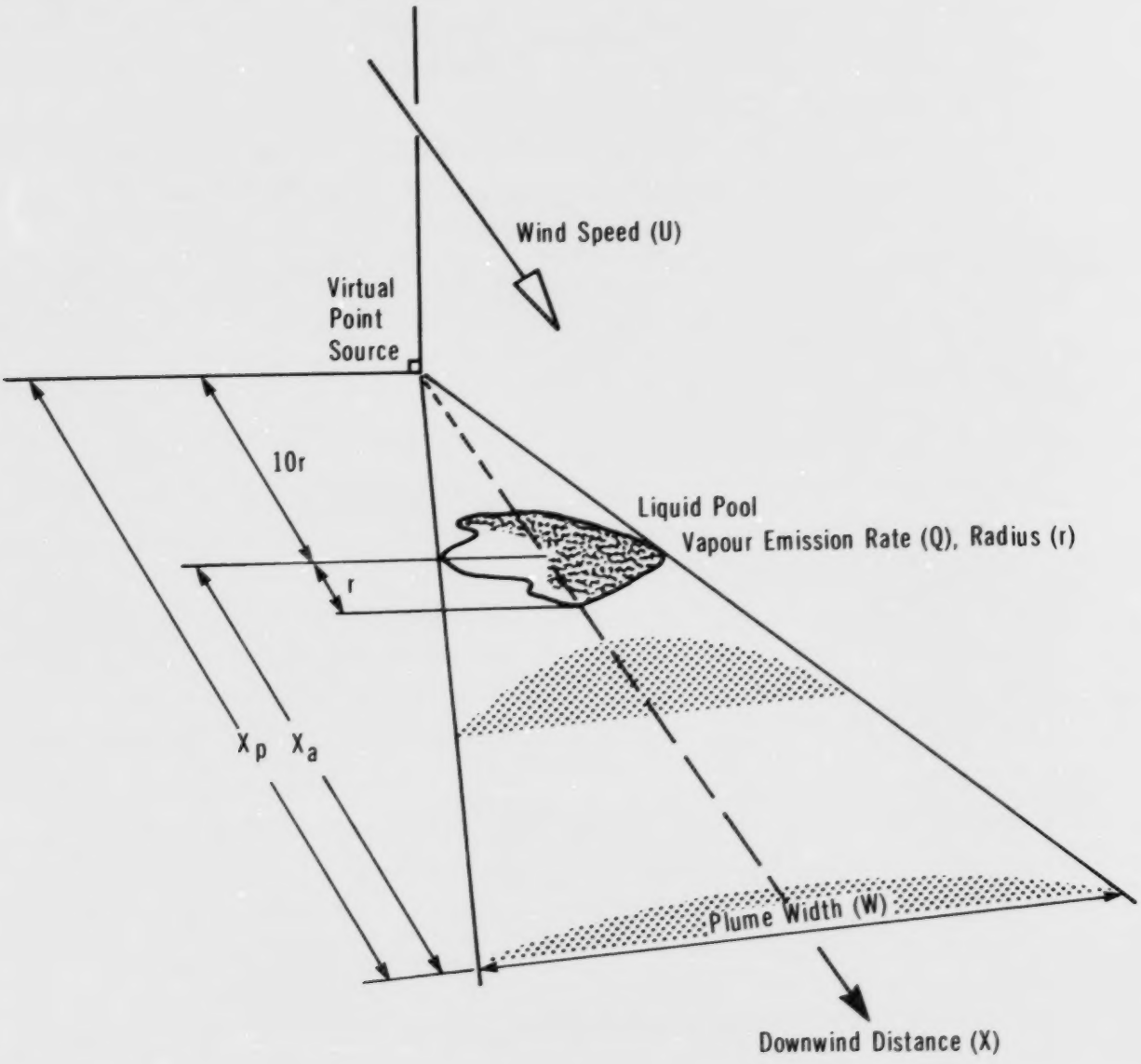
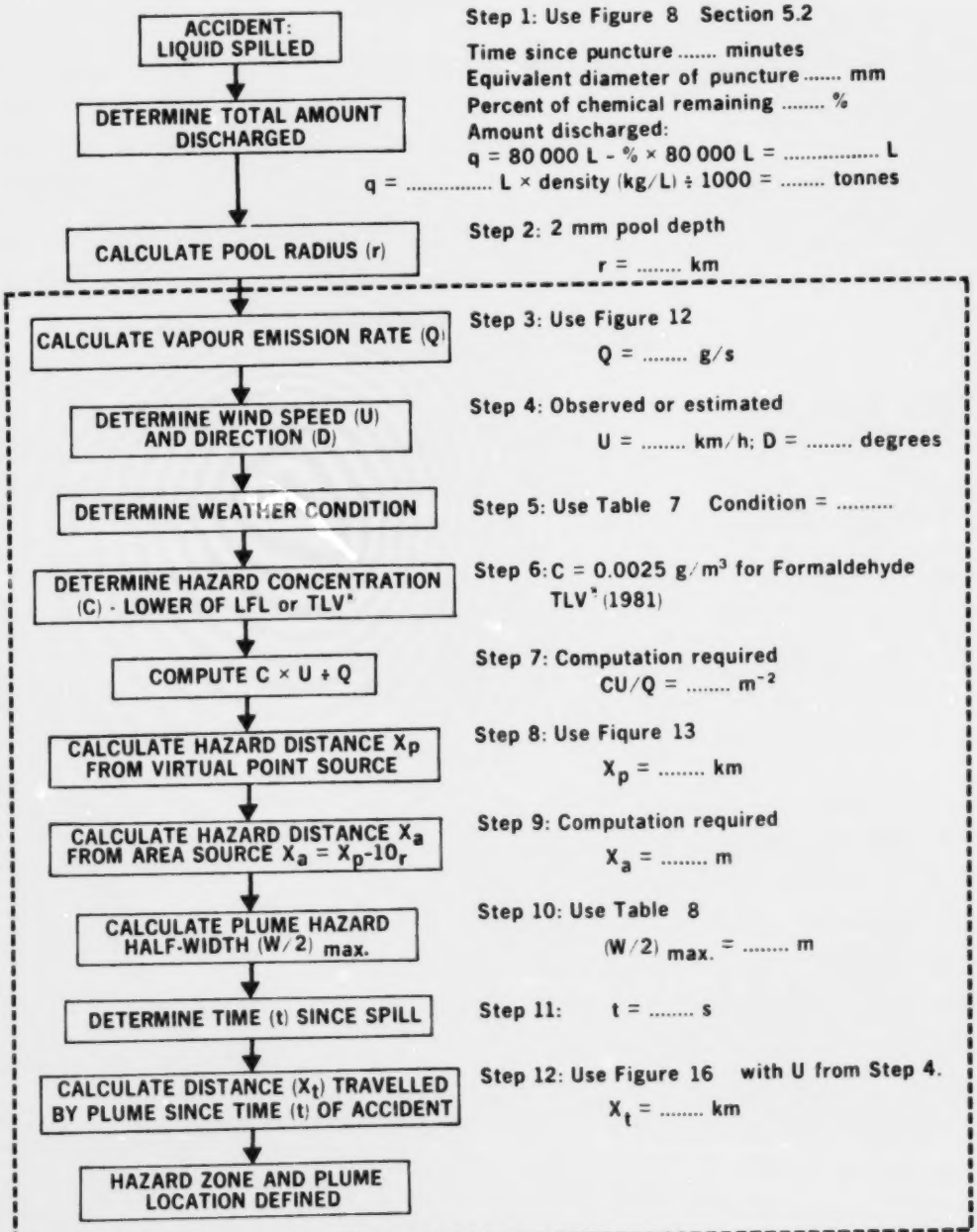


FIGURE 11

FORMALDEHYDE (37% SOLUTION)

FLOW CHART TO DETERMINE VAPOUR HAZARD ZONE


ACCIDENT: LIQUID SPILLED
DETERMINE TOTAL AMOUNT DISCHARGED
CALCULATE POOL RADIUS (r)
CALCULATE VAPOUR EMISSION RATE (Q)
DETERMINE WIND SPEED (U) AND DIRECTION (D)
DETERMINE WEATHER CONDITION
DETERMINE HAZARD CONCENTRATION (C) - LOWER OF LFL or TLV*
COMPUTE C × U ÷ Q
CALCULATE HAZARD DISTANCE Xp FROM VIRTUAL POINT SOURCE
CALCULATE HAZARD DISTANCE Xa FROM AREA SOURCE Xa = Xp-10r
CALCULATE PLUME HAZARD HALF-WIDTH (W/2) max.
DETERMINE TIME (t) SINCE SPILL
CALCULATE DISTANCE (Xt) TRAVELLED BY PLUME SINCE TIME (t) OF ACCIDENT
HAZARD ZONE AND PLUME LOCATION DEFINED

Step 1: Use Figure 8 Section 5.2

Time since puncture ..... minutes
Equivalent diameter of puncture ..... mm
Percent of chemical remaining ..... %
Amount discharged:
q = 80 000 L - % × 80 000 L = ... L
q = ... L × density (kg/L) ÷ 1000 = ... tonnes

Step 2: 2 mm pool depth

r = ... km

Step 3: Use Figure 12

Q = ... g/s

Step 4: Observed or estimated

U = ... km/h; D = ... degrees

Step 5: Use Table 7 Condition = ...

Step 6: C = 0.0025 g/m^3 for Formaldehyde TLV* (1981)

Step 7: Computation required

CU/Q = ... m^{-2}

Step 8: Use Fiqure 13

X_p = ... km

Step 9: Computation required

X_a = ... m

Step 10: Use Table 8

$(W/2)_{max.}$ = ... m

Step 11: t = ... s

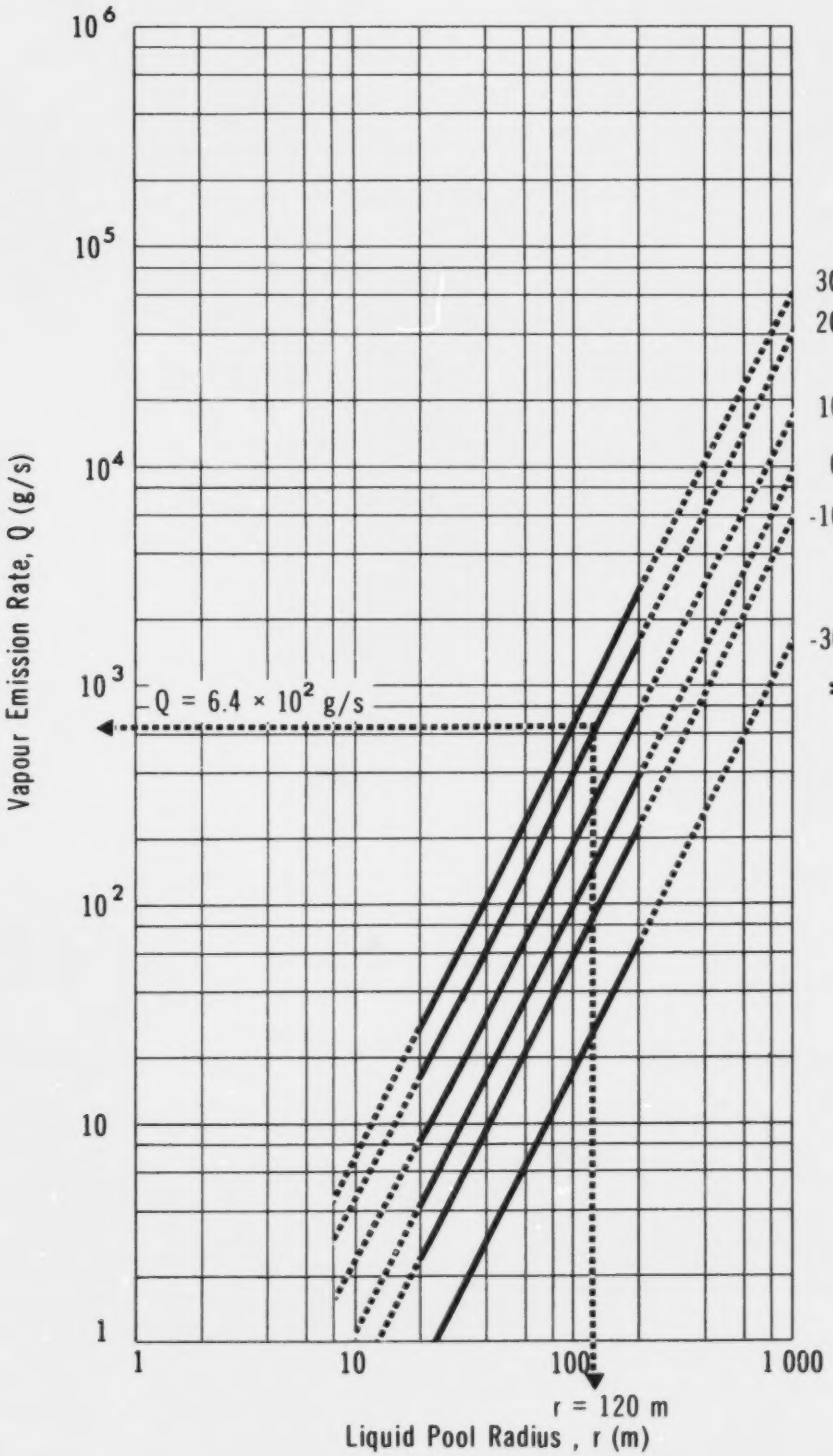
Step 12: Use Figure 16 with U from Step 4.

X_t = ... km

FIGURE 12

FORMALDEHYDE (37% SOLUTION)

VAPOUR EMISSION RATE VS LIQUID POOL RADIUS FOR VARIOUS TEMPERATURES



* Note: Nomogram applies for wind speed of 4.5 m/s. See Introduction Manual for relationships to compute values for other wind speeds, if necessary. Also, the solid portions of the curves represent spills of 0.05 to 86 tonnes.

evaporation rates with time. The use of the value at the initial formaldehyde concentration will therefore be the worst case situation.

Use: For a pool of formaldehyde solution of known radius, the rate (Q) at which formaldehyde vapour is released to the atmosphere at a given temperature can then be estimated from Figure 12. The solid portions of the curves represent spills of 0.05 to 86 tonnes, the latter representing about one standard 80 000 L rail car load of formaldehyde solution. It should be noted that Figure 12 is valid for a wind speed of 4.5 m/s (16.1 km/h) and therefore can only be used to provide an approximation of formaldehyde vapour emission rates at other wind speeds. The Introduction Manual contains the appropriate equation to convert the evaporation rate at 4.5 m/s to an evaporation rate at another wind speed should it be desired.

It should also be noted that the determination of the emission rate is based on the spill radius on calm water (Table VI, CHRIS 1974). The spill radius employed was arbitrarily chosen as an intermediate value between that of benzene (a moderately volatile liquid) and that of iso-amyl nitrite (a nonvolatile liquid). This model situation was chosen to apply for water-soluble liquids with boiling points above ambient temperature, and to a limited number of water-soluble and water-insoluble organic liquids that are not treated by CHRIS (CHRIS 1974). Since calm water represents a flat, unbounded surface compared to the type of ground surface that would normally be encountered in a spill situation (namely, irregular and porous), the spill radius on calm water is considered to provide the maximum value. Therefore, when spills on land are assessed by using the water algorithm, the spill radius would be overestimated and worst case values are provided.

5.3.2.2 Figure 13: Normalized vapour concentration versus downwind distance. Figure 13 shows the relationship between the vapour concentration and the downwind distance for weather conditions D and F. The nomograms were developed using the dispersion models described in the Introduction Manual. The vapour concentration is represented by the normalized, ground-level concentration (CU/Q) at the centreline of the contaminant plume. Weather condition F is the poorest for dispersing a vapour cloud and condition D is the most common in parts of Canada. Before using Figure 13, the weather condition must be determined from Table 7.

FIGURE 13

FORMALDEHYDE

NORMALIZED VAPOUR CONCENTRATION VS DOWNWIND DISTANCE

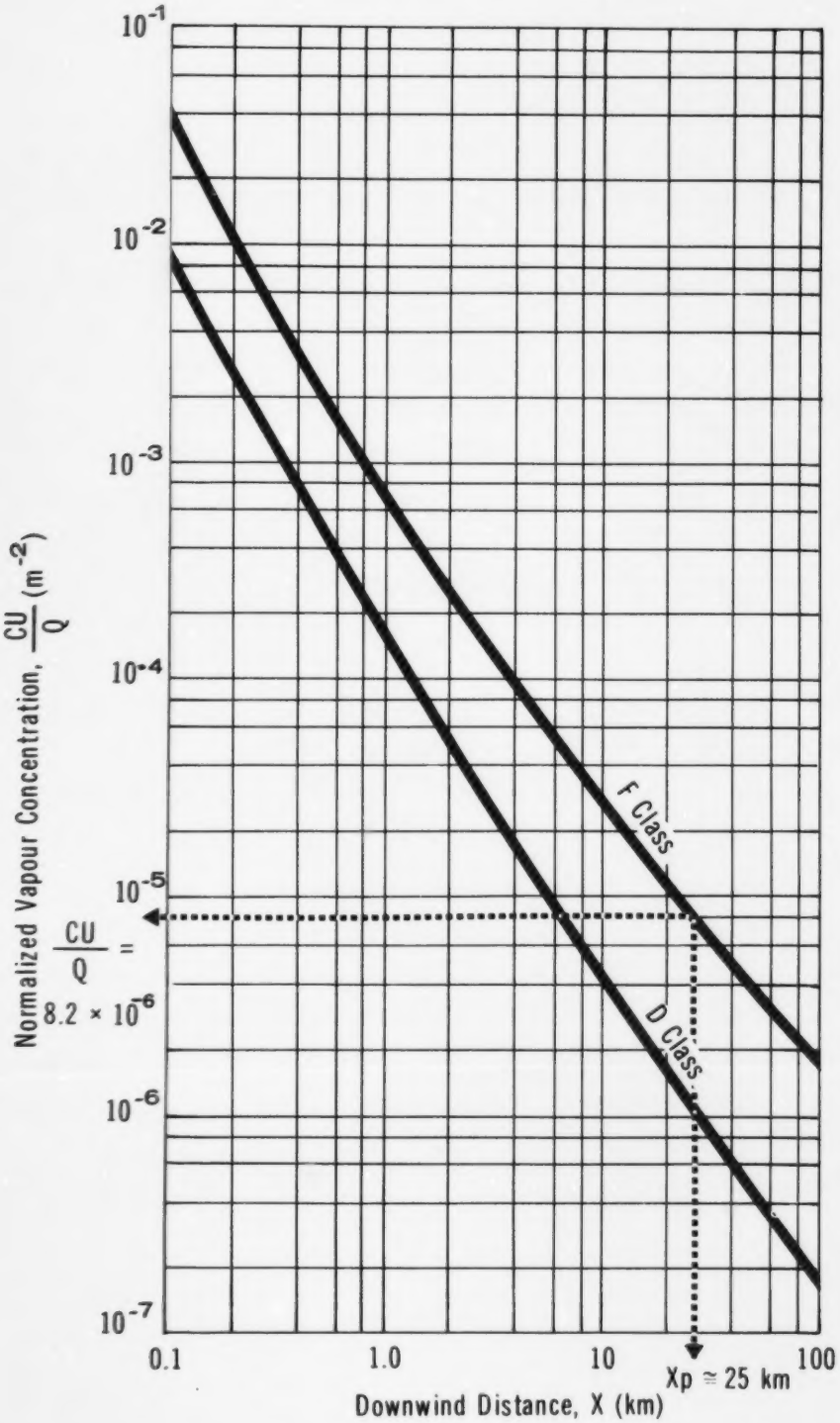


TABLE 7 WEATHER CONDITIONS

Weather Condition F	Weather Condition D
Wind speed <11 km/h (≃ 3 m/s) and one of the following: - overcast day - night time - severe temperature inversion	Most other weather conditions

Use: The maximum hazard distance, X_p, downwind of the spill can be calculated from Figure 13 knowing:

- Q, the vapour emission rate (g/s)
- U, the wind speed (m/s)
- the weather condition
- the hazard concentration limit, C, which is the lower value of the Threshold Limit Value (TLV•, in g/m^3), or the Lower Flammability Limit (LFL, in g/m^3). Note: To convert the TLV•, in ppm, and the LFL, in % by volume, to concentrations in g/m^3, use Figures 14 and 15

A hazard concentration limit of the TLV• has been chosen for formaldehyde (as opposed to a value of 10 times the TLV•) due to the likelihood that the present TLV• will be lowered as a result of the suspected carcinogenicity of formaldehyde. However, for calculation purposes, the present TLV• of 0.0015 g/m^3 has been used.

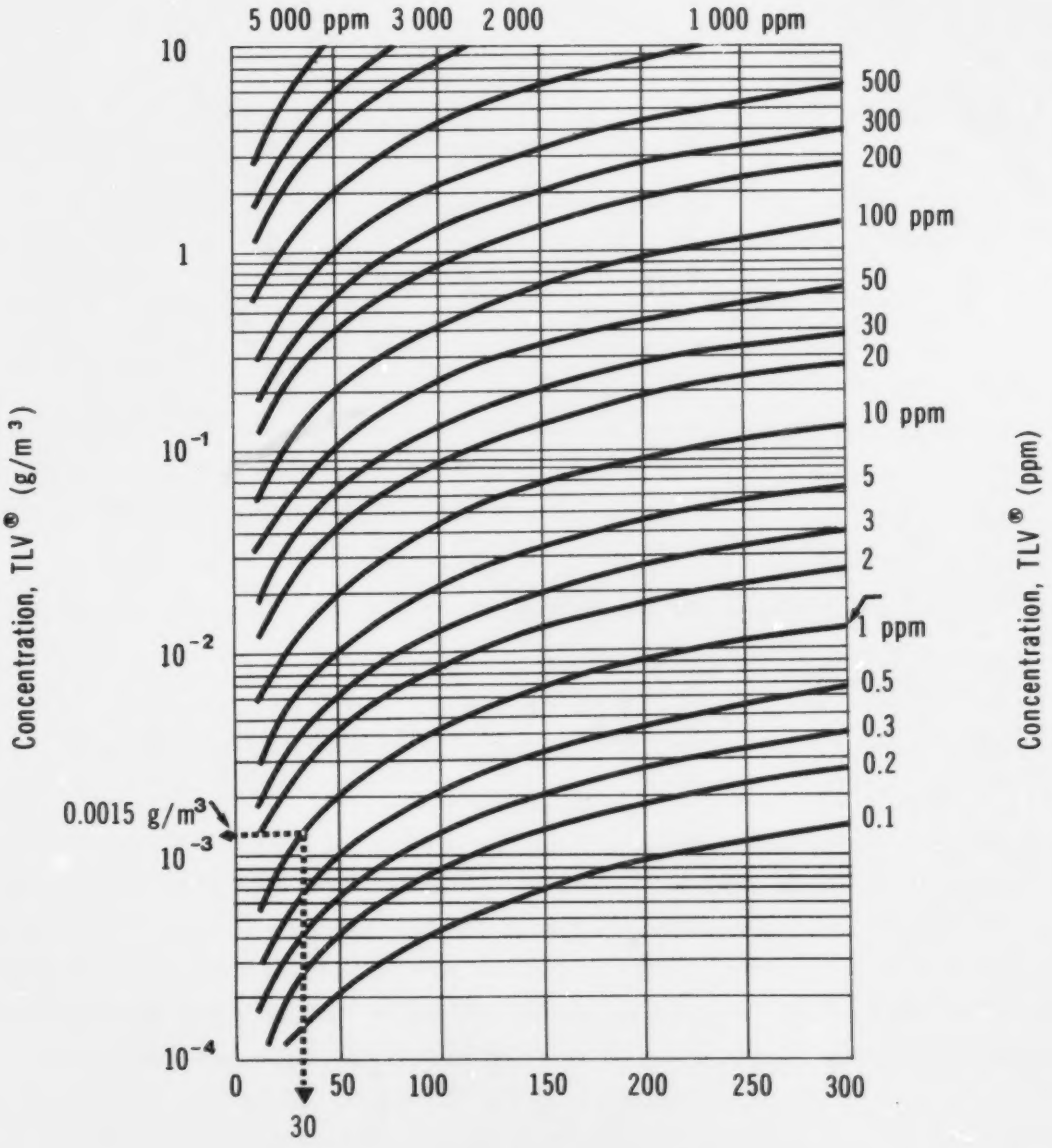
5.3.2.3 Table 8: Maximum plume hazard half-widths. This table presents data on the maximum plume hazard half-width, $(W/2)_{max}$, for a range of Q/U values under weather conditions D and F. These data were computed using the dispersion modelling techniques given in the Introduction Manual for a value of the formaldehyde Threshold Limit Value (TLV•) of 0.0015 g/m^3. The maximum plume hazard half-width represents the maximum half-width of the formaldehyde vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of the TLV•. Table 8 is therefore only applicable for a formaldehyde hazard concentration limit of the TLV•, or 0.0015 g/m^3. Also, data are provided up to a maximum hazard distance downwind of 100 km.

Under weather condition D, the wind speed (U) range applicable is 1 to 30 m/s. The range of vapour emission rates (Q) used was 300 to 17 500 g/s, corresponding to formaldehyde spills in the range of about 6 to 5000 tonnes, respectively. If the entire contents of an 80 000 L (17 600 Imp. gal.) tank car spill, the mass spilled would be

FIGURE 14

FORMALDEHYDE

CONVERSION OF THRESHOLD LIMIT VALUE (TLV®) UNITS (ppm to g/m³)



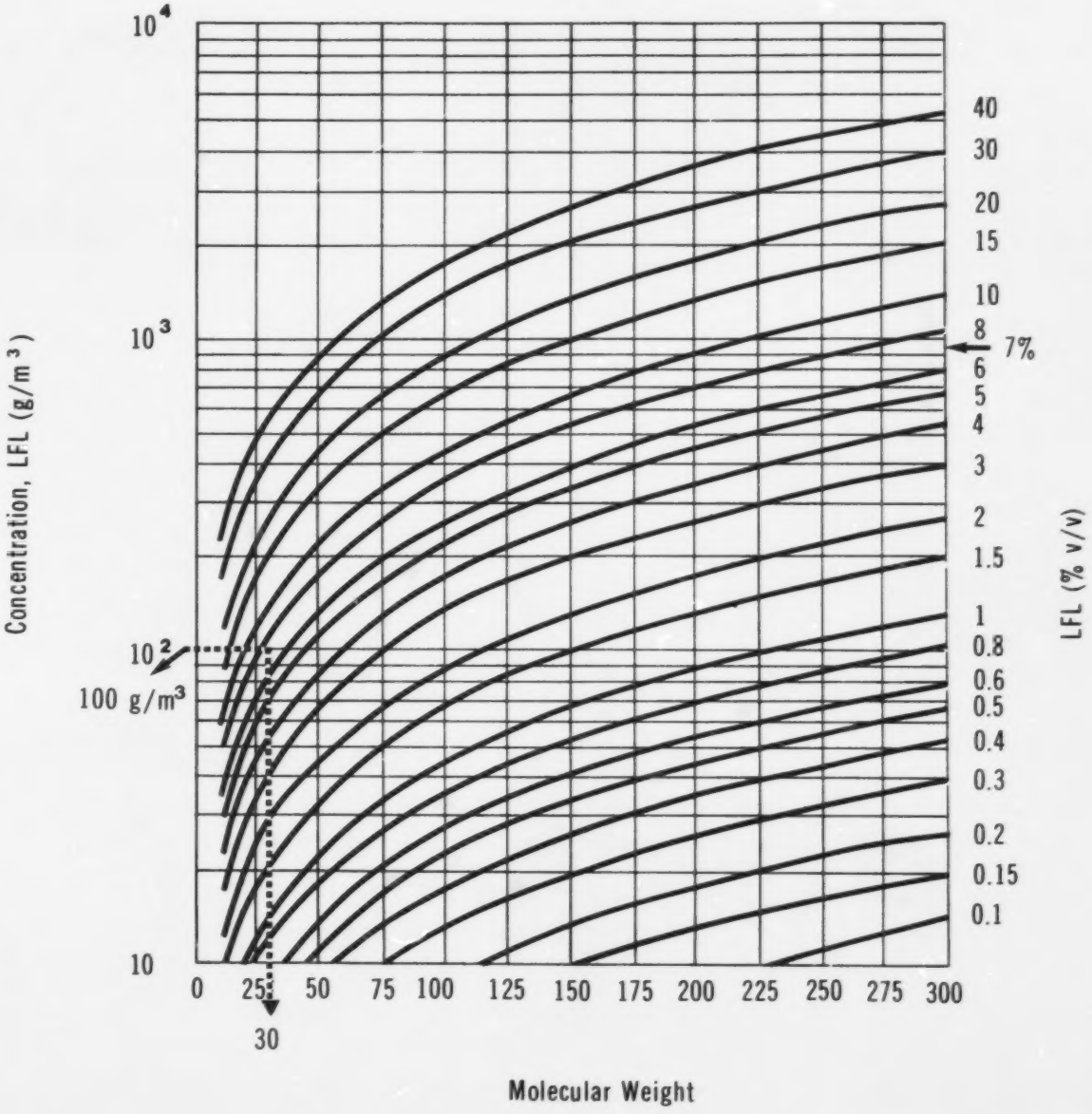
Example: Formaldehyde, MW=30, TLV® = 1 ppm MW = 30,
then TLV® in g/m³ = 0.0015

Note: Data applicable at 25°C and 760 mm Hg pressure

FIGURE 15

FORMALDEHYDE

CONVERSION OF LOWER FLAMMABILITY LIMIT (LFL) UNITS (volume % to g/m³)



Example: Formaldehyde, M = 30, LFL = 7% then LFL in g/m³ = 100

Note: data applicable at 25°C and 760 mm Hg pressure

TABLE 8 MAXIMUM PLUME HAZARD HALF-WIDTHS (FOR 37 PERCENT FORMALDEHYDE SOLUTION AT 20°C)

Weather Condition D			Weather Condition F		
Q/U (g/m)	$(W/2)_{max}$ (m)		Q/U (g/m)	$(W/2)_{max}$ (m)	
17 500	3430	(99.5 km)*	1500	1430	(99.5 km)*
15 000	3115		1250	1250	
12 500	2785		1000	1060	
10 000	2425		750	855	
7 500	2030		500	630	
5 000	1580	Q/U = 305 →	300	430	→ $(W/2)_{max}$ = 430
3 750	1320		250	375	
2 500	1030		200	325	
2 000	895		150	270	
1 500	750		100	210	
1 250	670		50	135	
1 000	585		25	85	
750	500		10	50	
500	395				
300	290				
250	260				
200	230				
150	195				
100	155				
50	100				
25	70				
10	40				

* Data are provided up to a maximum downwind hazard distance of 100 km.

Example: A spill releasing formaldehyde vapour at the rate of Q = 640 g/s under weather condition F and a wind speed U = 2.1 m/s means Q/U = 305 g/m which results in a maximum plume hazard half-width $(W/2)_{max}$ = 430 m.

Note: Above table is valid only for a formaldehyde concentration of the TLV®, or 0.0015 g/m^3.

86 400 kg, or approximately 86 tonnes. Therefore, under class D of Table 8, data are provided for up to 58 times this amount.

Under weather condition F, the wind speed (U) range applicable is 1 to 3 m/s. The range of vapour emission rates (Q) used was 30 to 1500 g/s, corresponding to formaldehyde spills in the range of about 0.3 to 80 tonnes, respectively. Therefore, under class F of Table 8, data are provided for almost one standard rail car load.

Use: Knowing the weather condition, Q and U, compute Q/U. Choose the closest Q/U value in the table and the corresponding $(W/2)_{max}$, the maximum plume

hazard half-width, in metres. (For an intermediate value, interpolate Q/U and $(W/2)_{max}$ values.) Also refer to the example at the bottom of Table 8.

5.3.2.4 **Figure 16: Plume travel time versus travel distance.** Figure 16 presents plots of plume travel time (t) versus plume travel distance (X_t) as a function of different wind speeds (U). This is simply the graphical presentation of the relationship $X_t = Ut$ for a range of typical wind speeds.

Use: Knowing the time (t) since the spill occurred and the wind speed (U), the distance (X_t) can be determined which indicates how far downwind the plume has travelled.

5.3.3 **Sample Calculation.** The sample calculation given below is intended to outline the steps required to estimate the downwind hazard zone which could result from a spill of liquid formaldehyde. The user is cautioned to take note of the limitations in the calculation procedures described herein and in the Introduction Manual. The estimates provided here apply only for conditions given. It is recommended that the user employ known or observational estimates (i.e., of the spill radius) in a particular spill situation if possible.

Problem:

During the night, at about 2:00 a.m., 20 tonnes of formaldehyde were spilled on a flat ground surface. It is now 2:05 a.m. The temperature is 20°C and the wind is from the NW at 7.5 km/h. Determine the extent of the vapour hazard zone.

Solution

Step 1: Quantity spilled is given, q = 20 tonnes

Step 2: Determine the pool radius (r) for a spill of 20 tonnes

- Use the observed (measured) pool radius if possible. If not, use the maximum radius calculated assuming a 2 mm spill thickness
- Radius (r) = 120 m ÷ 1000 = 0.12 km

Step 3: Calculate the vapour emission rate (Q) at T = 20°C

- From Figure 12, for r = 120 m and T = 20°C, Q = 6.4×10^2 g/s

Step 4: Determine the wind speed (U) and direction (D)

- Use available weather information, preferably on-site observations
- Given:

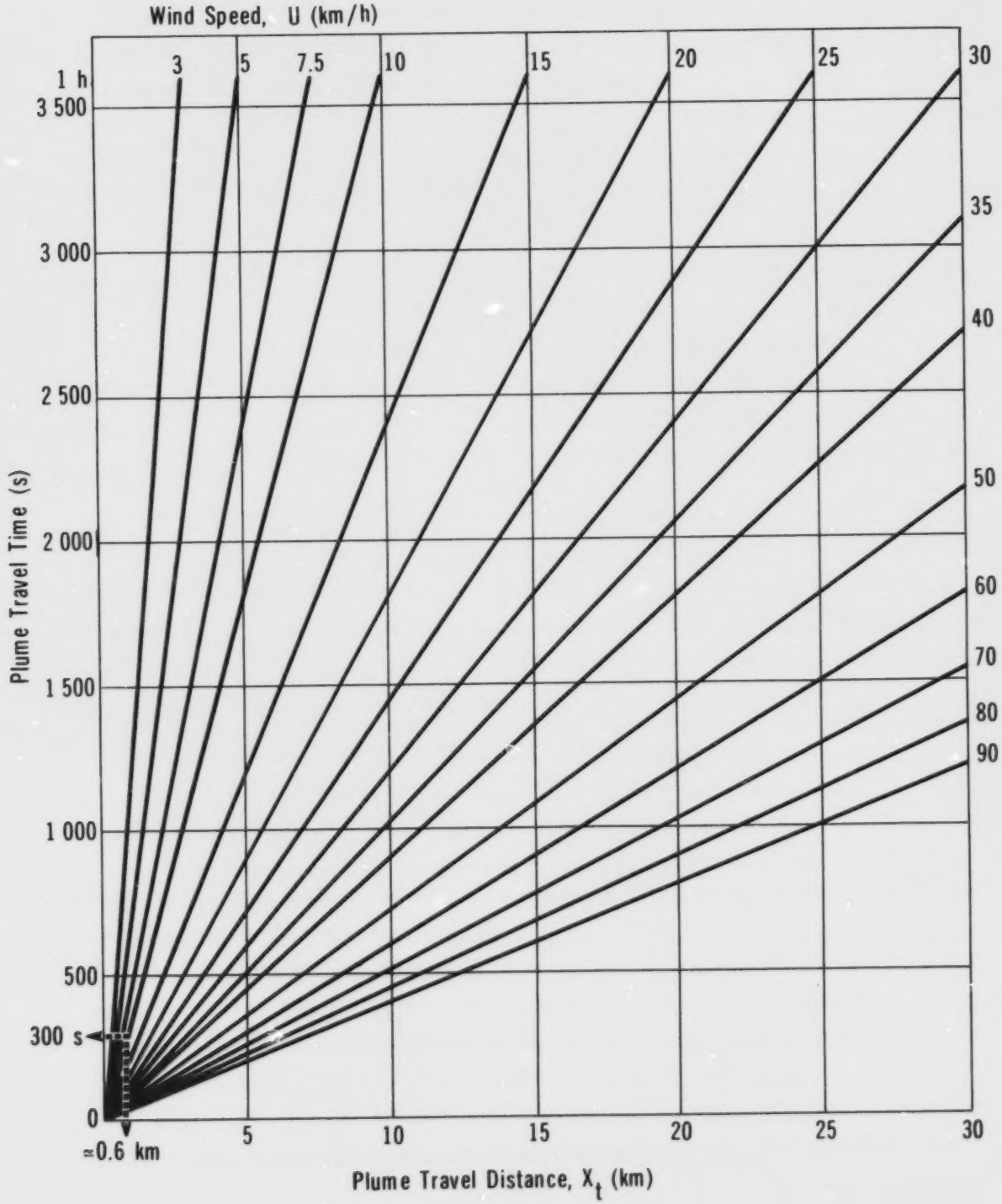
  U = 7.5 km/h, then U = 7.5 ÷ 3.6 = 2.1 m/s

  D = NW or 315° (D = Direction from which wind is blowing)

FIGURE 16

FORMALDEHYDE

PLUME TRAVEL TIME VS TRAVEL DISTANCE



Step 5: Determine the weather condition

- From Table 7, weather condition = F since U is less than 11 km/h and it is night

Step 6: Determine the hazard concentration limit (C)

- This is the lower of the TLV• or the LFL, so for formaldehyde
  $C = 0.0015\ g/m^3$ ($TLV• = 0.0015\ g/m^3$; $LFL = 100\ g/m^3$)

Step 7: Compute CU/Q

- $CU/Q = \dfrac{0.0025 \times 2.1}{640} = 8.2 \times 10^{-6}\ m^{-2}$

Step 8: Calculate the downwind distance (X_p) from the virtual point source

- From Figure 13, with $CU/Q = 8.2 \times 10^{-6}\ m^{-2}$ and weather condition F, $X_p \approx 25$ km

Step 9: Calculate the hazard distance (X_a) downwind of the area source

- With $X_p = 25$ km and $r = 0.12$ km, then
  $X_a = X_p - 10\ r = 25\ km - 10\ (0.12\ km) = 23.8$ km

Step 10: Calculate the plume hazard half-width $(W/2)_{max}$

- Use Table 8
- With $Q = 640$ g/s and $U = 2.1$ m/s, then $Q/U = \dfrac{640}{2.1} = 305$ g/m

  Then for weather condition F, the closest Q/U value is 300 g/m which gives $(W/2)_{max} \approx 430$ m

Step 11: Determine the time since the spill

- $t = 5\ min \times 60 = 300$ s

Step 12: Calculate the distance travelled (X_t) by the vapour plume since the time of the accident

- Using Figure 16, with $t = 300$ s and $U = 7.5$ km/h, then $X_t = 0.6$ km (more accurately from $Ut = 2.1\ m/s \times 300\ s = 630\ m = 0.63\ km$)

Step 13: Map the hazard zone

- This is done by drawing a rectangular area with dimensions of twice the maximum plume hazard half-width (430 m) by the maximum hazard distance downwind of the area source (23.8 km) along the direction of the wind, as shown in Figure 17

FIGURE 17

FORMALDEHYDE

HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM

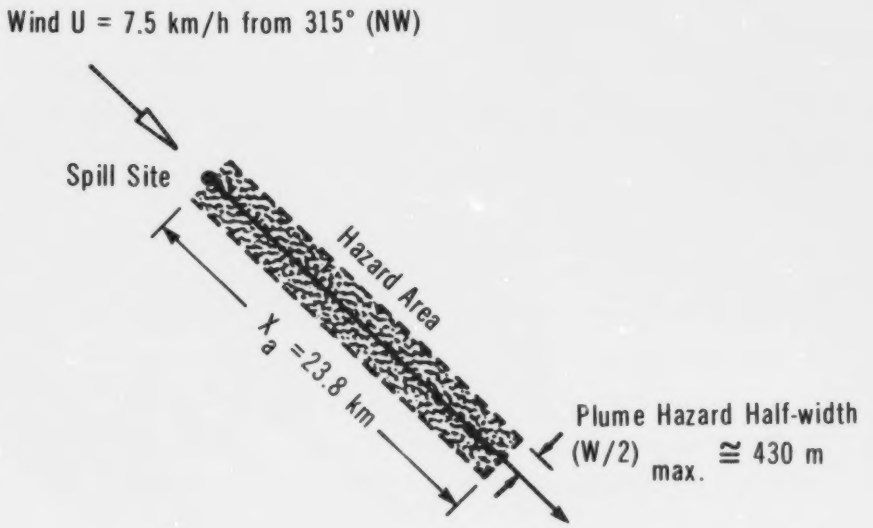
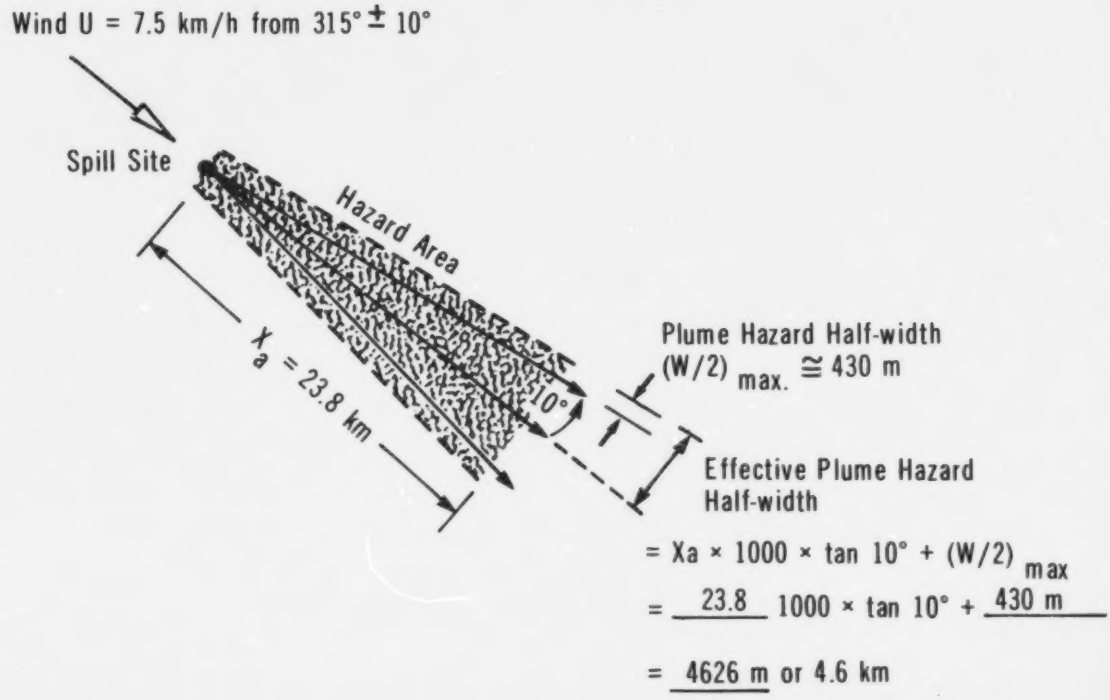


FIGURE 18

FORMALDEHYDE

HAZARD AREA FOR UNSTEADY WINDS, EXAMPLE PROBLEM


Wind U = 7.5 km/h from 315° ± 10°
Spill Site
Hazard Area
X_a = 23.8 km
10°
Plume Hazard Half-width
$(W/2)_{max.} \cong$ 430 m
Effective Plume Hazard Half-width
= Xa × 1000 × tan 10° + $(W/2)_{max}$
= 23.8 1000 × tan 10° + 430 m
= 4626 m or 4.6 km

- If the wind is reported to be fluctuating by 20° about 315° (or from 315° ± 10°), the hazard zone is defined as shown in Figure 18
- Note that the plume has only travelled 0.63 km in the 5 minutes since the spill. At a wind speed of 7.5 km/h, there remain 185 minutes before the plume reaches the maximum downwind hazard distance of 23.8 km

5.4 Behaviour in Water

5.4.1 Introduction. Formaldehyde is miscible in water. When spilled on water, formaldehyde solution mixes with water on contact and the spill is diluted. This mixing can generally be described by classical diffusion equations with one or more diffusion coefficients. In rivers, the principal mixing agent is stream turbulence while in calm water mixing takes place by molecular diffusion.

To estimate the pollutant concentration in a river downstream from a spill, the turbulent diffusion has been modelled. The one-dimensional model uses an idealized rectangular channel section and assumes a uniform concentration of the pollutant throughout the section. Obviously, this applies only to points sufficiently far downstream of the spill where mixing and dilution have distributed the pollutant across the entire river channel. The model is applicable to rivers where the ratio of width to depth is less than 100 ($W/d < 100$) and assumes a Manning's roughness coefficient of 0.03. Details of the model are outlined in the Introduction Manual.

No modelling has been carried out for molecular diffusion in still water. Rather, nomograms have been prepared to define the hazard zone and the average concentration within the hazard zone as a function of spill size, but independent of time.

5.4.2 Nomograms. The following nomograms are presented to calculate pollutant concentrations in non-tidal rivers and in lakes (still water).

Non-tidal Rivers

Figure 20: time versus distance for a range of average stream velocities

Figure 21: hydraulic radius versus channel width for a range of stream depths

Figure 22: diffusion coefficient versus hydraulic radius for a range of average stream velocities

Figure 23: alpha* versus diffusion coefficient for various time intervals

Figure 24: alpha versus delta* for a range of spill sizes

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* Alpha and delta are conversion factors only and are of no significance other than to facilitate calculation of downstream concentration.

Figure 25: maximum concentration versus delta for a range of river cross-sectional areas

Lakes or Still Water Bodies

Figure 26: volume versus radius for the hazard zone for a range of lake depths

Figure 27: average concentrations versus volume for the hazard zone for a range of spill sizes

The flowchart in Figure 19 outlines the steps required to estimate the downstream concentration after a spill and identifies the nomograms to be used. These nomograms (Figure 20 through 27) are described in the following subsections.

5.4.2.1 Nomograms for non-tidal rivers.

Figure 20: Time versus distance. Figure 20 presents a simple relationship between average stream velocity, time, and distance. Using an estimate of average stream velocity (U), the time (t) to reach any point of interest at some distance (X) downstream of the spill can be readily obtained from Figure 20.

Figure 21: Hydraulic radius versus channel width. The model used to estimate downstream pollutant concentration is based on an idealized rectangular channel of width (W) and depth (d).

The hydraulic radius (r) for the channel is required in order to estimate the longitudinal diffusion coefficient (E). The hydraulic radius (r) is defined as the stream cross-sectional area (A) divided by the wetted perimeter (P). Figure 21 is a nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

Figure 22: Diffusion coefficient versus hydraulic radius. Figure 22 permits calculation of the longitudinal diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 21 and the average stream velocity (U).

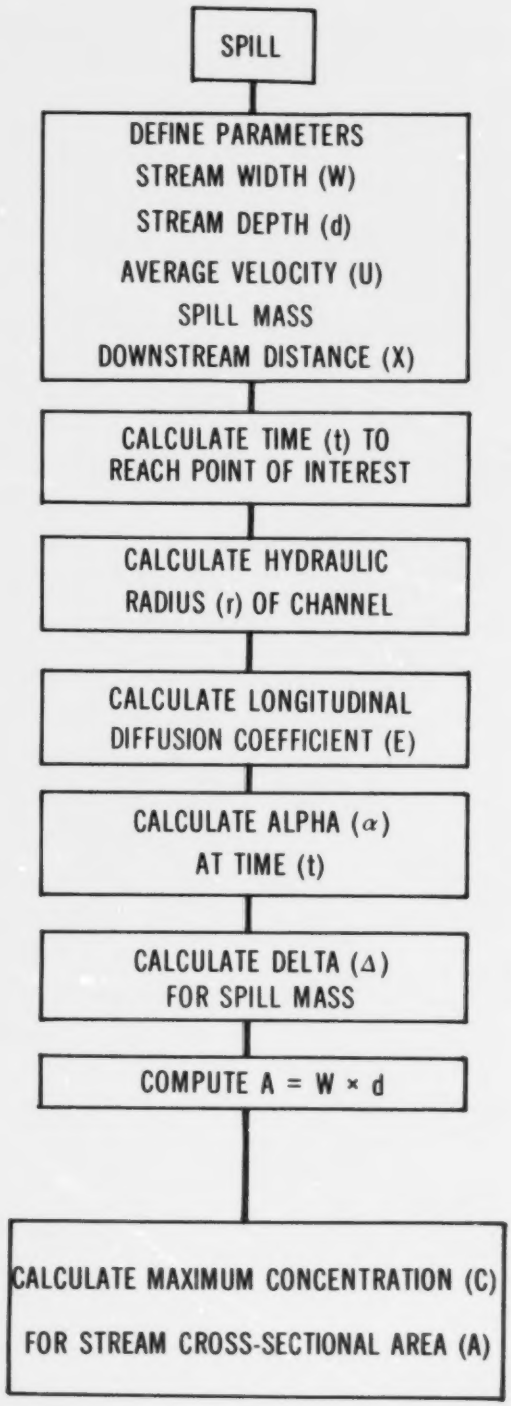
Figure 23: Alpha versus diffusion coefficient. Figure 23 is used to estimate a conversion factor, alpha (α), which is a function of the diffusion coefficient (E) and the time (t) to reach the point of interest downstream of the spill.

Figure 24: Alpha versus delta. A second conversion factor, delta (Δ), must be estimated from Figure 24 to allow determination of the pollutant concentration at the point of interest. Delta (Δ) is a function of alpha (α) and the spill size.

FIGURE 19

FORMALDEHYDE

FLOW CHART TO DETERMINE POLLUTANT CONCENTRATION IN NON-TIDAL RIVERS


SPILL
DEFINE PARAMETERS
STREAM WIDTH (W)
STREAM DEPTH (d)
AVERAGE VELOCITY (U)
SPILL MASS
DOWNSTREAM DISTANCE (X)
CALCULATE TIME (t) TO REACH POINT OF INTEREST
CALCULATE HYDRAULIC RADIUS (r) OF CHANNEL
CALCULATE LONGITUDINAL DIFFUSION COEFFICIENT (E)
CALCULATE ALPHA (α) AT TIME (t)
CALCULATE DELTA (Δ) FOR SPILL MASS
COMPUTE A = W × d
CALCULATE MAXIMUM CONCENTRATION (C) FOR STREAM CROSS-SECTIONAL AREA (A)

Step 1: Observed or Estimated

W = _____ m

d = _____ m

U = _____ m/s

MASS = _____ tonnes

X = _____ m

Step 2: Use Figure 20

t = _____ minutes

Step 3: Use Figure 21

r = _____ m

Step 4: Use Figure 22

E = _____ m^2/s

Step 5: Use Figure 23

α = _____

Step 6: Use Figure 24

Δ = _____

Step 7: Compute stream cross-sectional Area (A)

A = W × d _____ m^2

Step 8: Use Figure 25

C = _____ ppm

FIGURE 20

FORMALDEHYDE

TIME vs DISTANCE

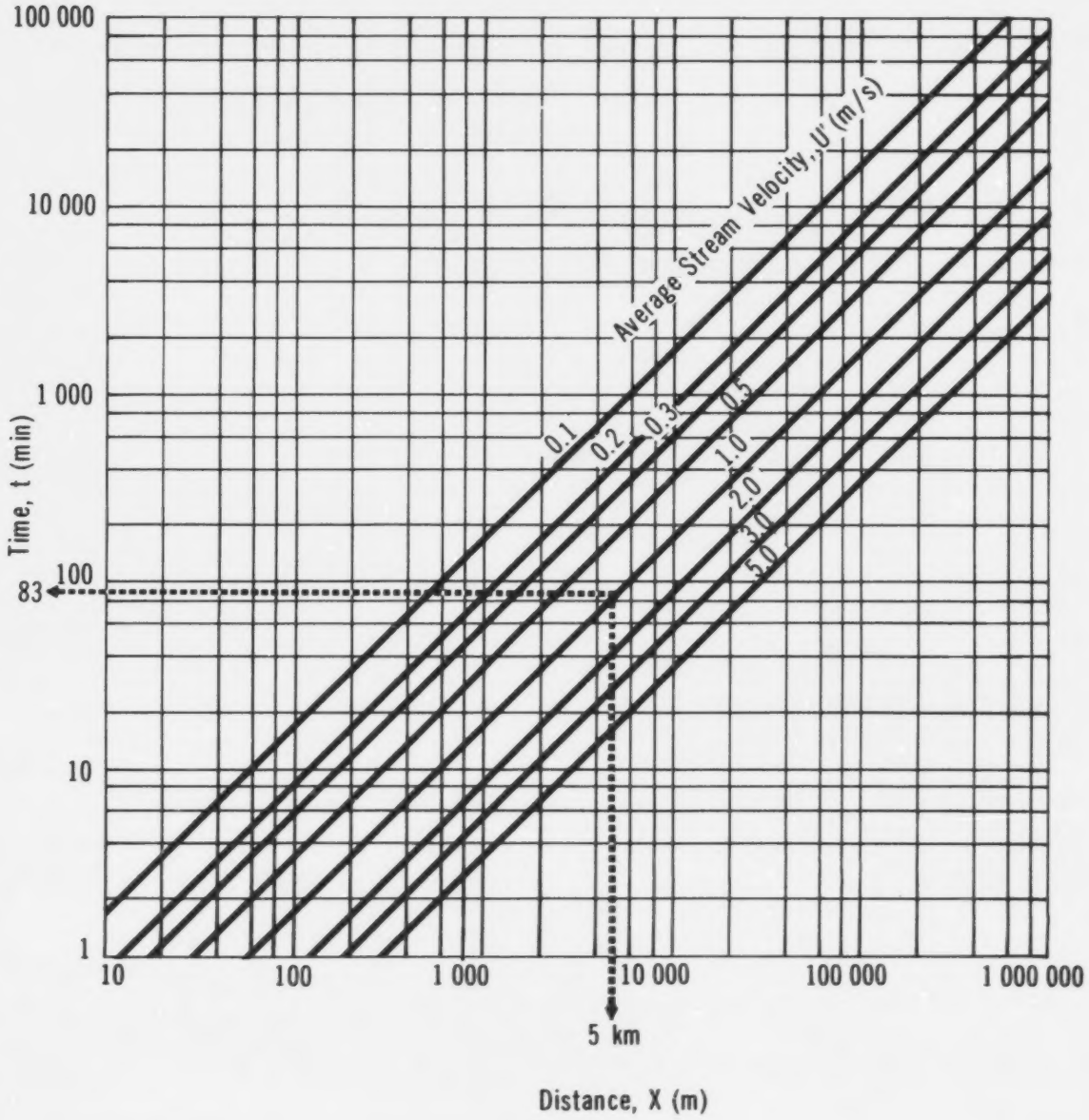


FIGURE 21

FORMALDEHYDE

HYDRAULIC RADIUS VS CHANNEL WIDTH

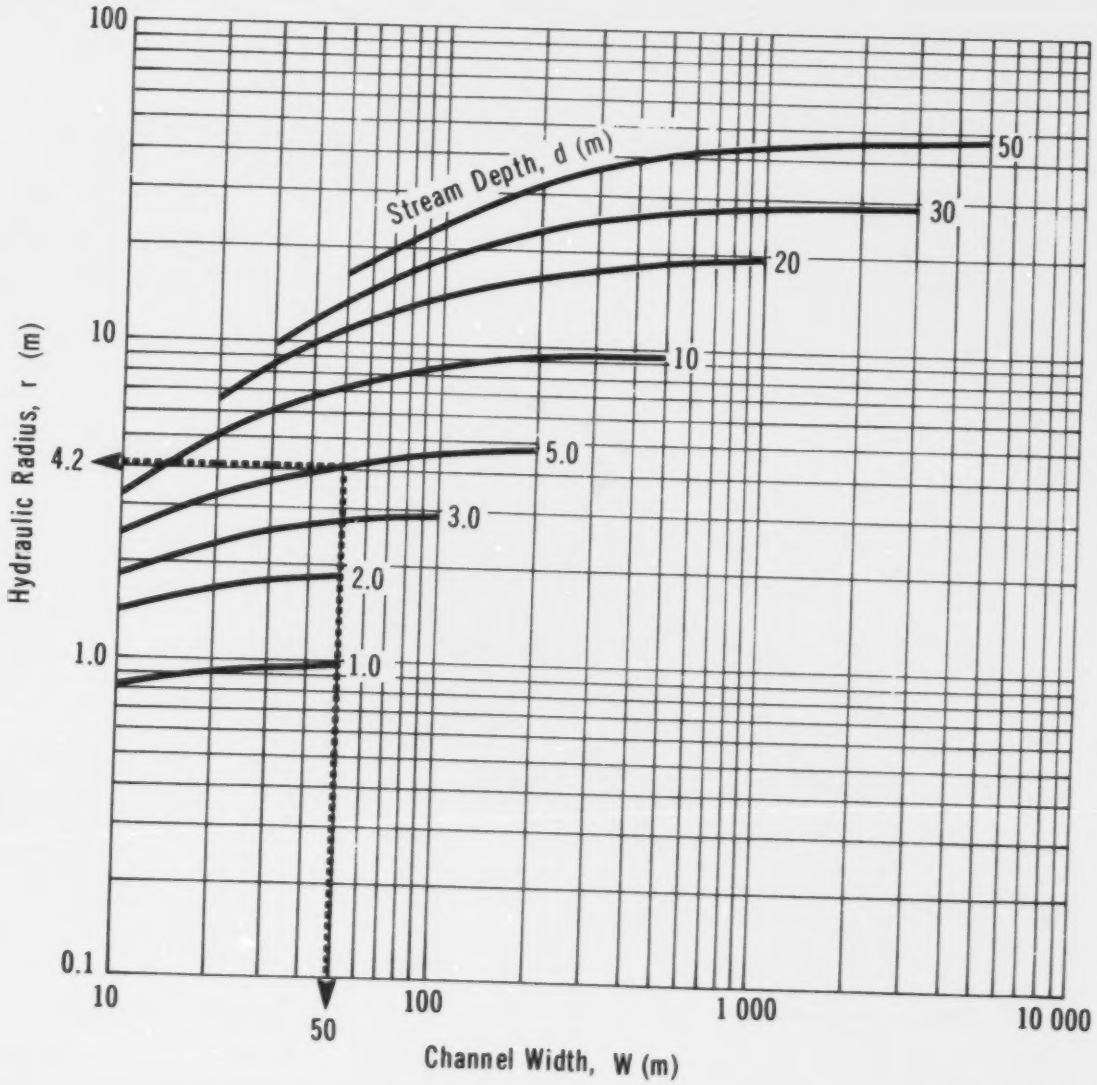


FIGURE 22

FORMALDEHYDE

DIFFUSION COEFFICIENT VS HYDRAULIC RADIUS

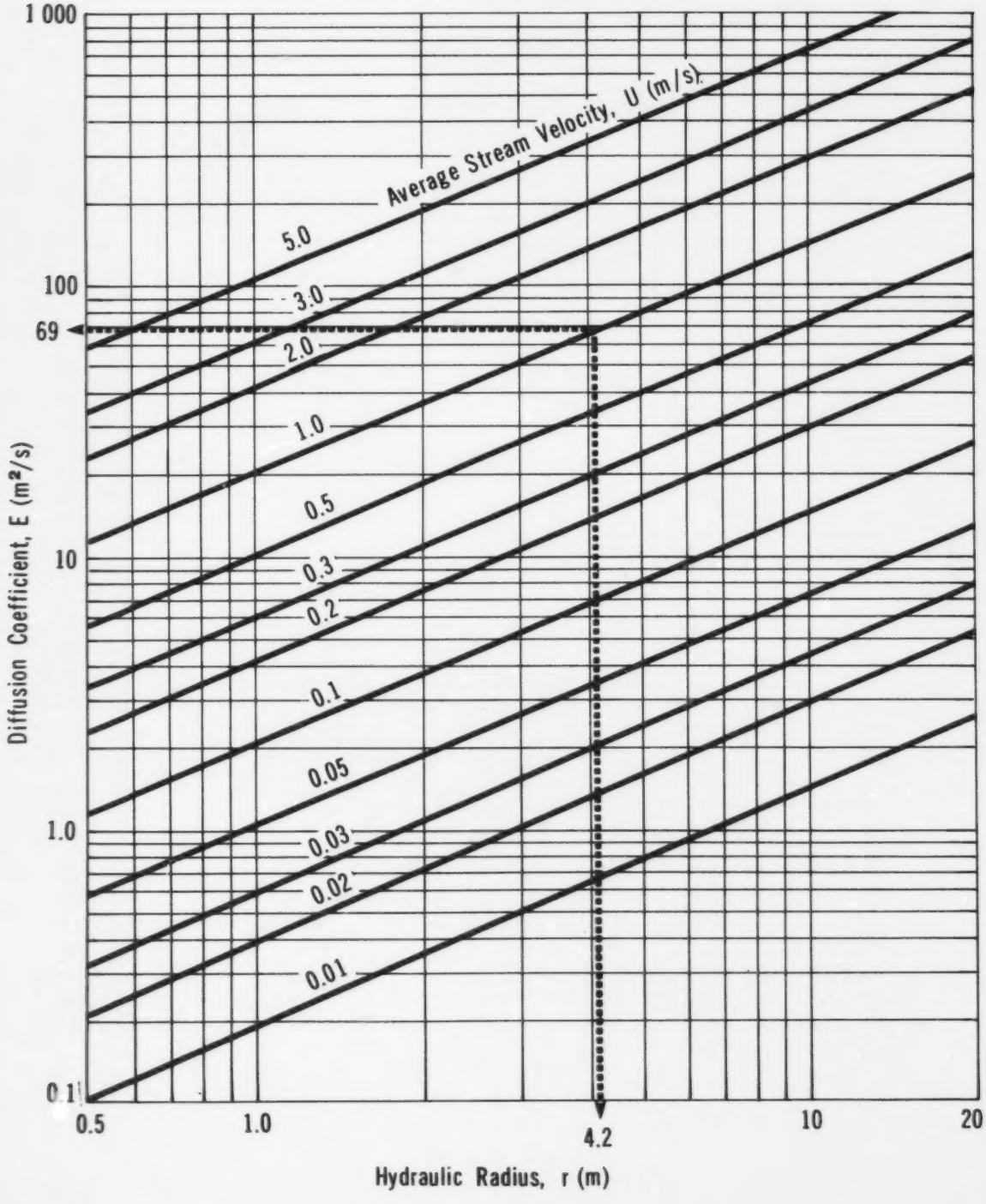


FIGURE 23

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ALPHA vs DIFFUSION COEFFICIENT

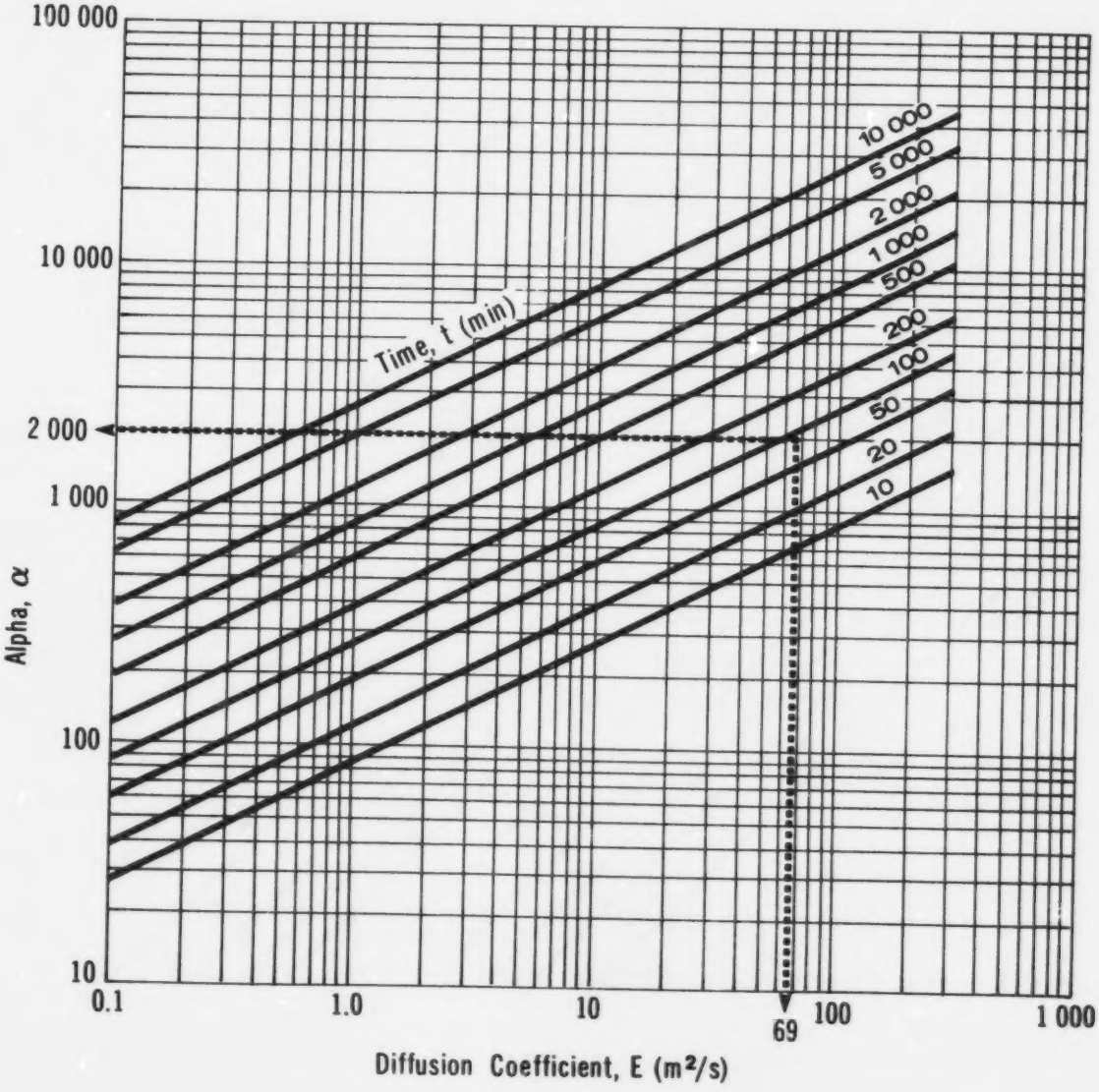

FIGURE 24

FORMALDEHYDE

ALPHA vs DELTA

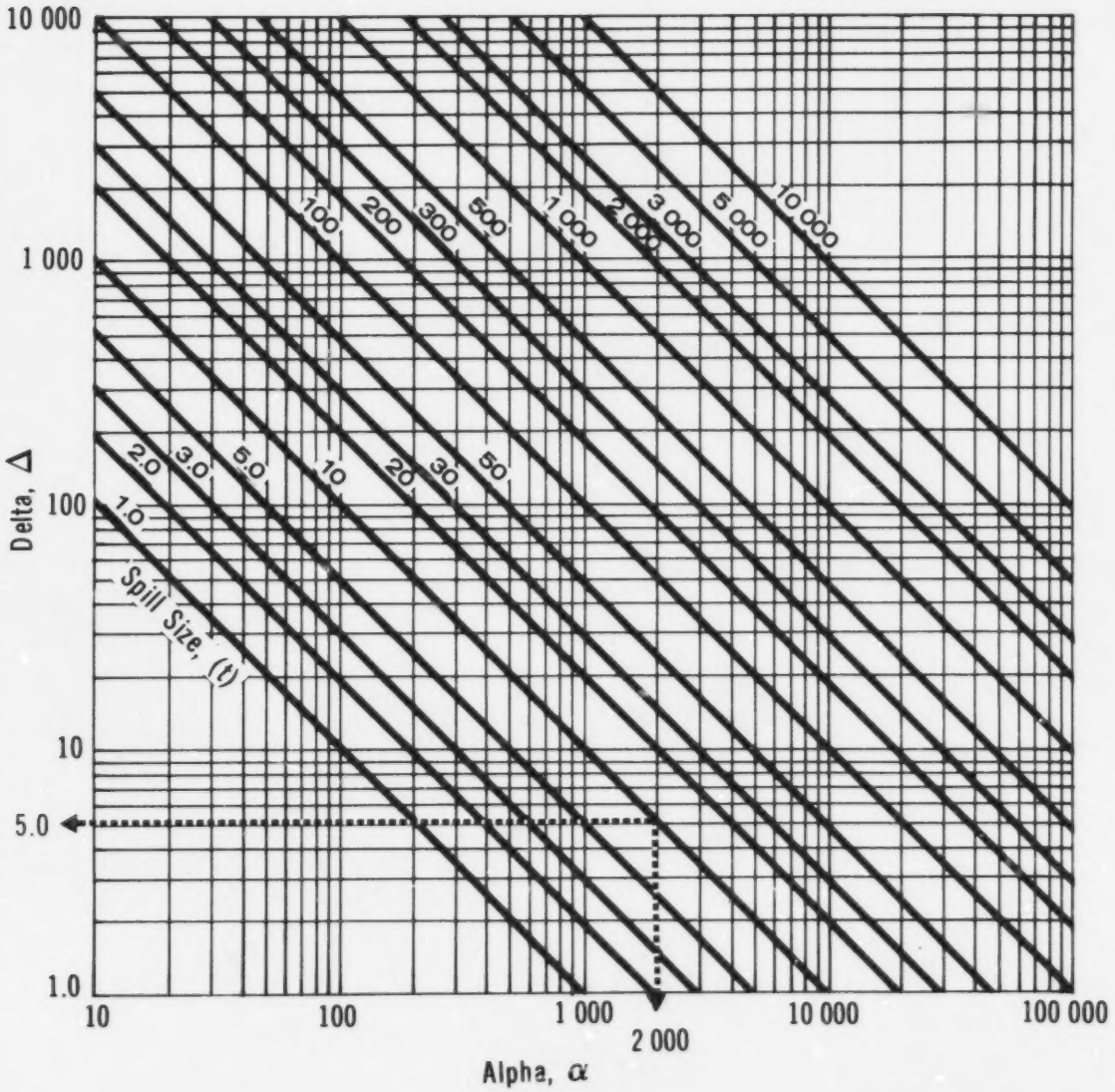

Figure 25: Maximum concentration versus delta. Figure 25 represents the final step for calculation of the maximum downstream pollutant concentration (C) at the point of interest. Using the factor delta (Δ) and knowing the stream cross-sectional area (A), the concentration (C) is readily obtained from the nomogram. The value obtained from Figure 25 applies to neutrally buoyant liquids or solids and will vary somewhat for other pollutants which are heavier or lighter than water.

5.4.2.2 Nomograms for lakes or still water bodies.

Figure 26: Volume versus radius. The spill of a neutrally buoyant liquid in a lake in the absence of wind and current has been idealized as a cylinder of radius (r) and length (d), equivalent to the depth of the lake at the point of spill. The volume of water in the cylinder can be obtained from Figure 26. The radius (r) represents the distance from the spill to the point of interest.

Figure 27: Average concentration versus volume. For a known volume of water (within the idealized cylinder of radius (r) and length (d)), the average concentration of pollutant (C) can be obtained from Figure 27 for a known mass of spill. This assumes the pollutant is spread evenly throughout the cylinder. For pollutants that are more or less dense than water, the actual concentration at the bottom would be higher or lower, respectively.

5.4.3 Sample Calculations.

5.4.3.1 Pollutant concentration in non-tidal rivers. A 20 tonne spill of 50 percent formaldehyde solution has occurred in a river. The stream width is 50 m and the stream depth is 5 m. The average stream velocity is estimated at 1 m/s. What is the maximum concentration expected at a water intake located 5 km downstream?

Solution

Step 1: Define parameters

- W = 50 m
- d = 5 m
- U = 1 m/s
- spill mass = 20 tonnes of 50 percent solution, equivalent to 10 tonnes of formaldehyde

Step 2: Calculate the time to reach the point of

- Use Figure 20
- With X = 5000 m and U = 1 m/s,

FIGURE 25

FORMALDEHYDE

MAXIMUM CONCENTRATION vs DELTA

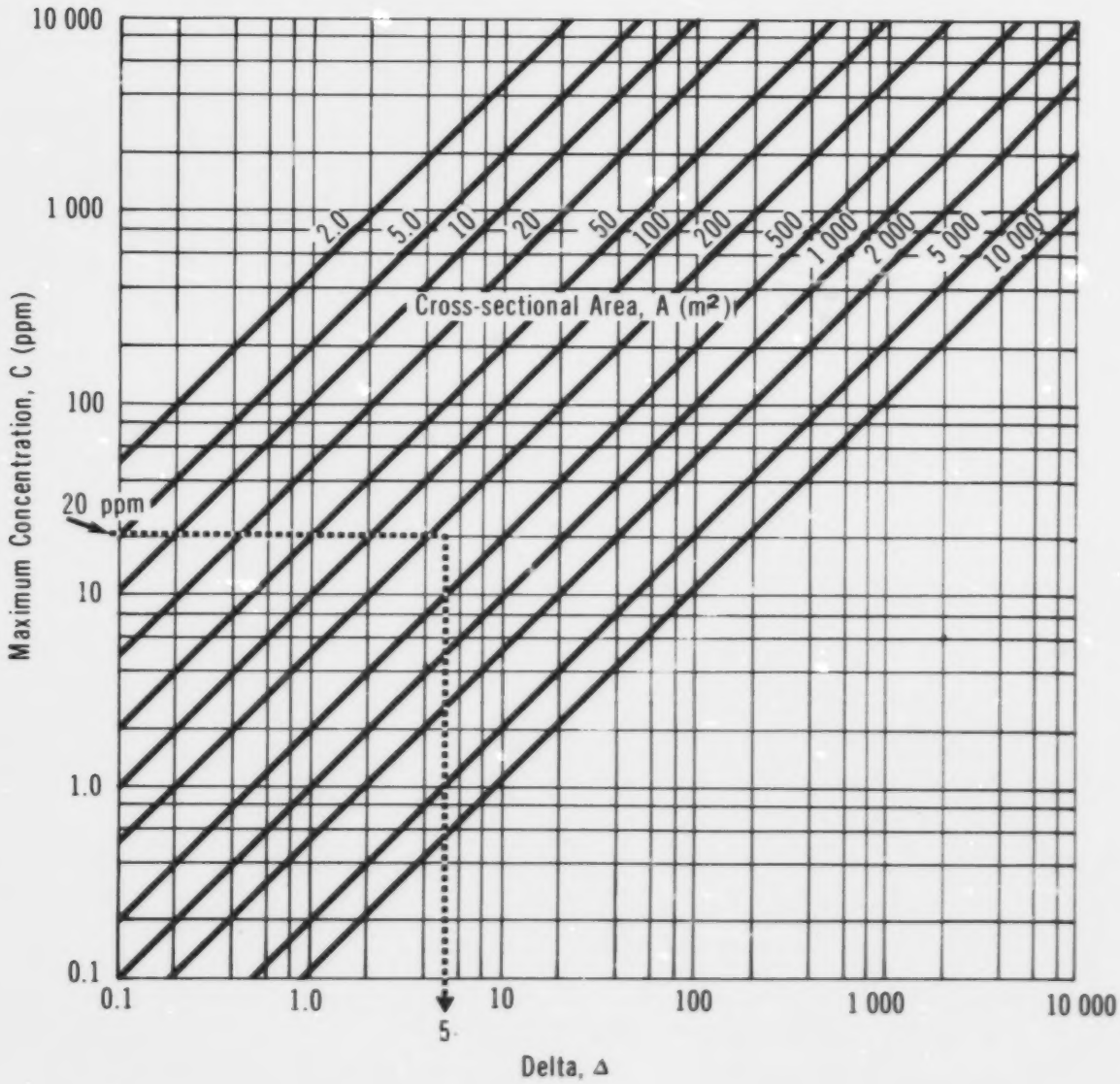

FIGURE 26

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VOLUME vs RADIUS

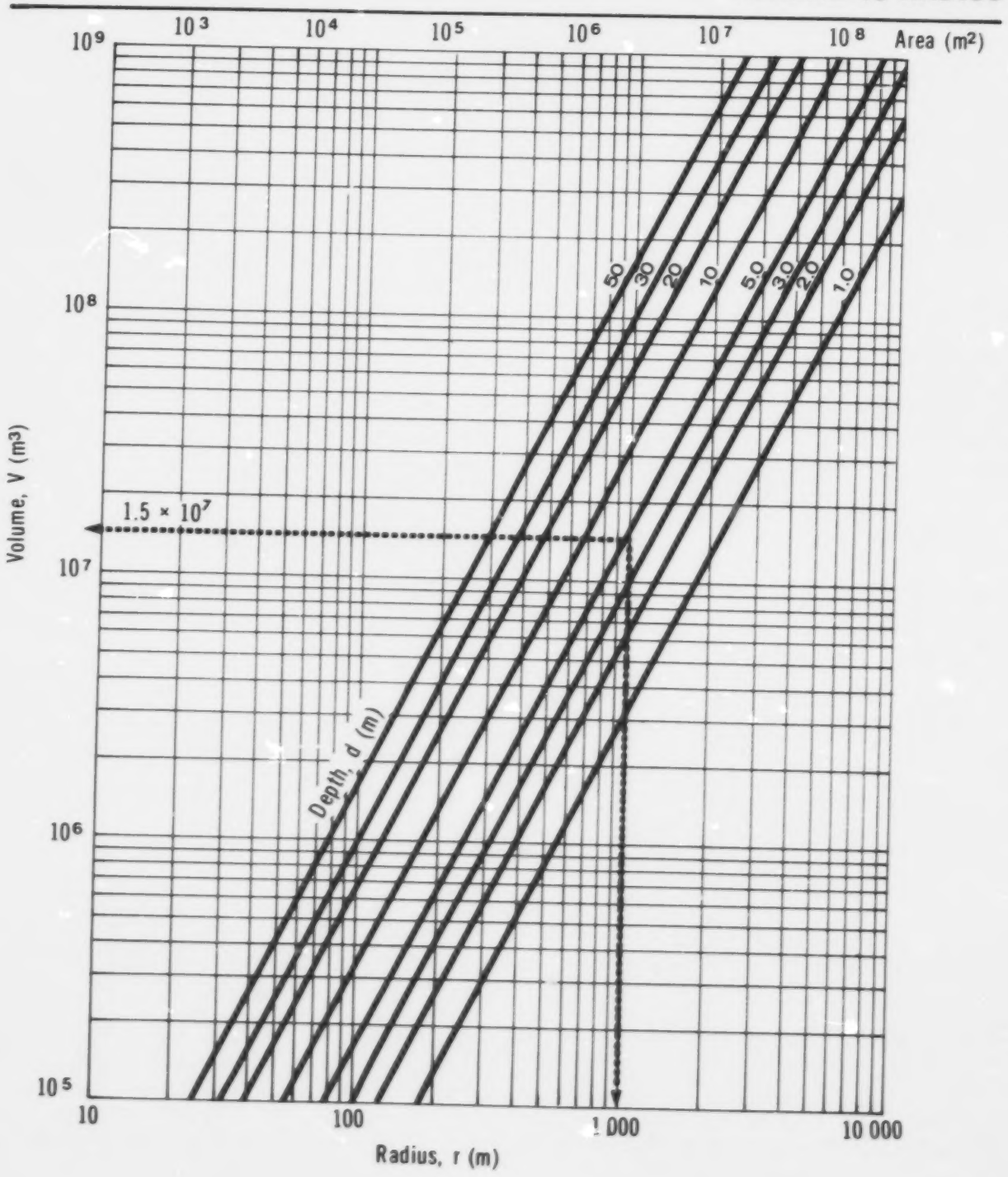

FIGURE 27

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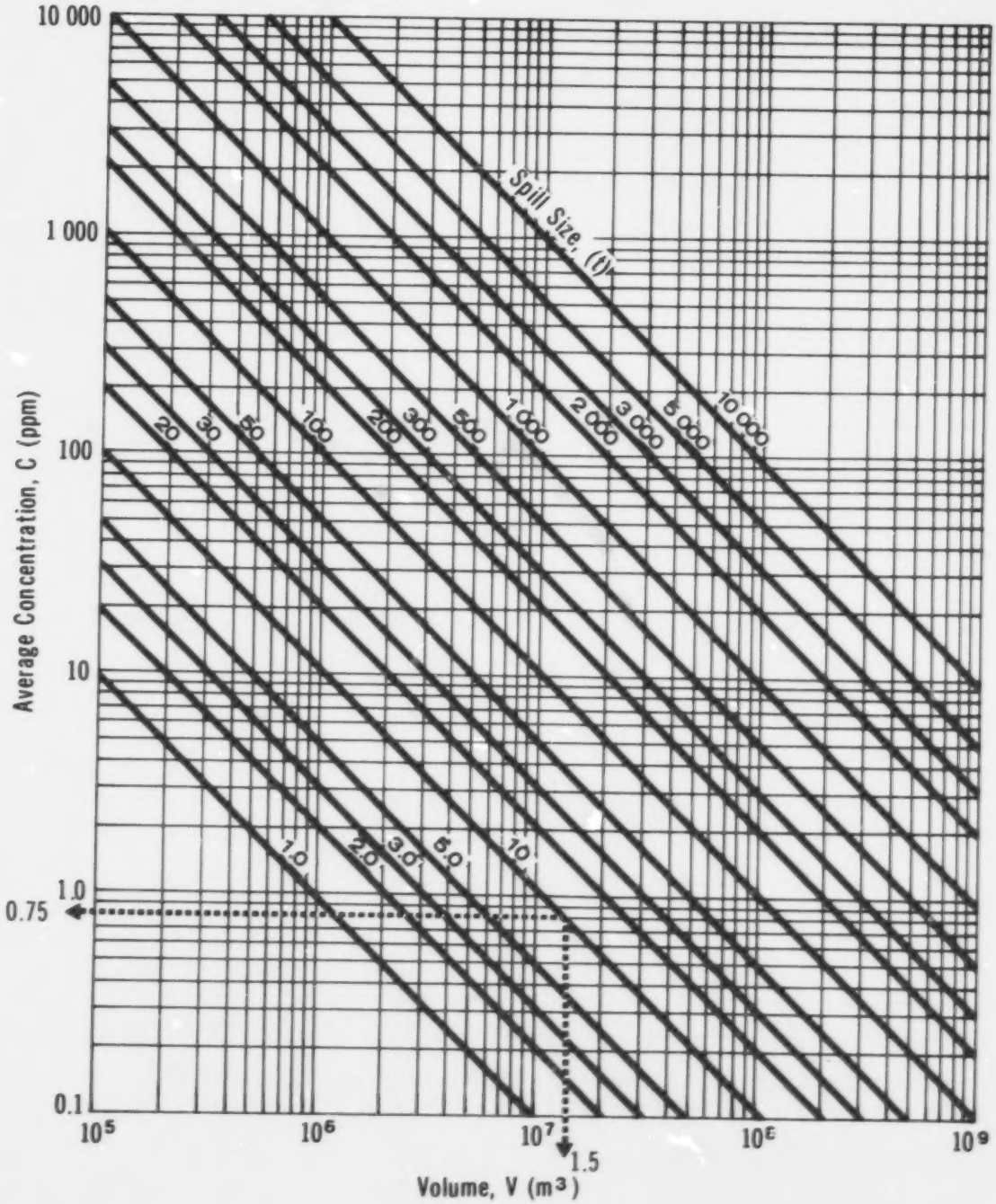
AVERAGE CONCENTRATION vs VOLUME



Step 3: Calculate the hydraulic radius (r)

- Use Figure 21
- With W = 50 m and d = 5 m, r = 4.2 m

Step 4: Calculate the longitudinal diffusion coefficient (E)

- Use Figure 22
- With r = 4.2 m and U = 1 m/s, E = 69 m^2/s

Step 5: Calculate alpha (α)

- Use Figure 23
- With E = 69 m^2/s and t = 83 min, α = 2000

Step 6: Calculate delta (Δ)

- Use Figure 24
- With alpha (α) = 2000 and spill mass = 10 tonnes, delta (Δ) = 5

Step 7: Compute the stream cross-sectional area (A)

- A = W x d = 50 x 5 = 250 m^2

Step 8: Calculate the maximum concentration (C) at the point of interest

- Use Figure 25
- With Δ = 5 and A = 250 m^2, C = 20 ppm

5.4.3.2 **Average pollutant concentration in lakes or still water bodies.** A 20 tonne spill of 50 percent formaldehyde solution has occurred in a lake. The point of interest is located on the shore approximately 1000 m from the spill. The average depth between the spill site and the point of interest is 5 m. What is the average concentration which could be expected?

Solution

Step 1: Define parameters

- d = 5 m
- r = 1000 m
- spill mass = 10 tonnes (equivalent amount of formaldehyde)

Step 2: Determine the volume of water available for dilution

- Use Figure 26
- With r = 1000 m, d = 5 m, the volume is approximately 1.5 x 10^7 m^3

Step 3: Determine the average concentration

- Use Figure 27
- With V = 1.5 x 10^7 m^3 and spill mass = 10 tonnes, the average concentration is 0.75 ppm

5.5 Subsurface Behaviour: Penetration into Soil

5.5.1 Mechanisms. The principles of contaminant transport in soil and their application to this work are presented in the Introduction Manual. Special considerations related to the spill of formaldehyde solution onto soil and its transport downward through the soil are presented here.

Formaldehyde solution consists of 30 to 52 percent formaldehyde and up to 15 percent methanol in water. This solution mixes with water and, if spilled onto soil, will infiltrate readily. Precipitation falling at the time of the spill or water used to flush the site will dilute the solution, thus enhancing infiltration. If the soil surface is saturated with moisture at the time of the spill, as might be the case after a rainfall, the spilled chemical will run off or remain ponded.

For this work, the soils have been assumed to be at field capacity (the maximum amount the soil will hold after excess is drained). This situation provides very little interstitial water to dilute the chemical during transport or to impede its downward movement and thus represents "worst case" analysis. During transport through the soil, formaldehyde can interact with the soil material, in particular through adsorption. However, significant amounts are expected to remain for transport down toward the groundwater table. The analysis used here neglects this retarding factor. Upon reaching the groundwater table, the contaminant will continue to move, now in the direction of groundwater flow. A contaminated plume will be produced, with dilution and diffusion serving to reduce the concentrations. This is shown schematically in Figure 28.

5.5.2 Equations Describing Formaldehyde Movement into Soil. The equations and assumptions used to describe contaminant movement downward through the unsaturated soil zone toward the groundwater table have been described in the Introduction Manual. Transport velocities have been based on Darcy's Law assuming saturated piston flow.

5.5.3 Saturated Hydraulic Conductivity of Formaldehyde in Soil. The saturated hydraulic conductivity (K_o), in m/s, is given by:

$$K_o = \frac{(\rho g)k}{\mu}$$

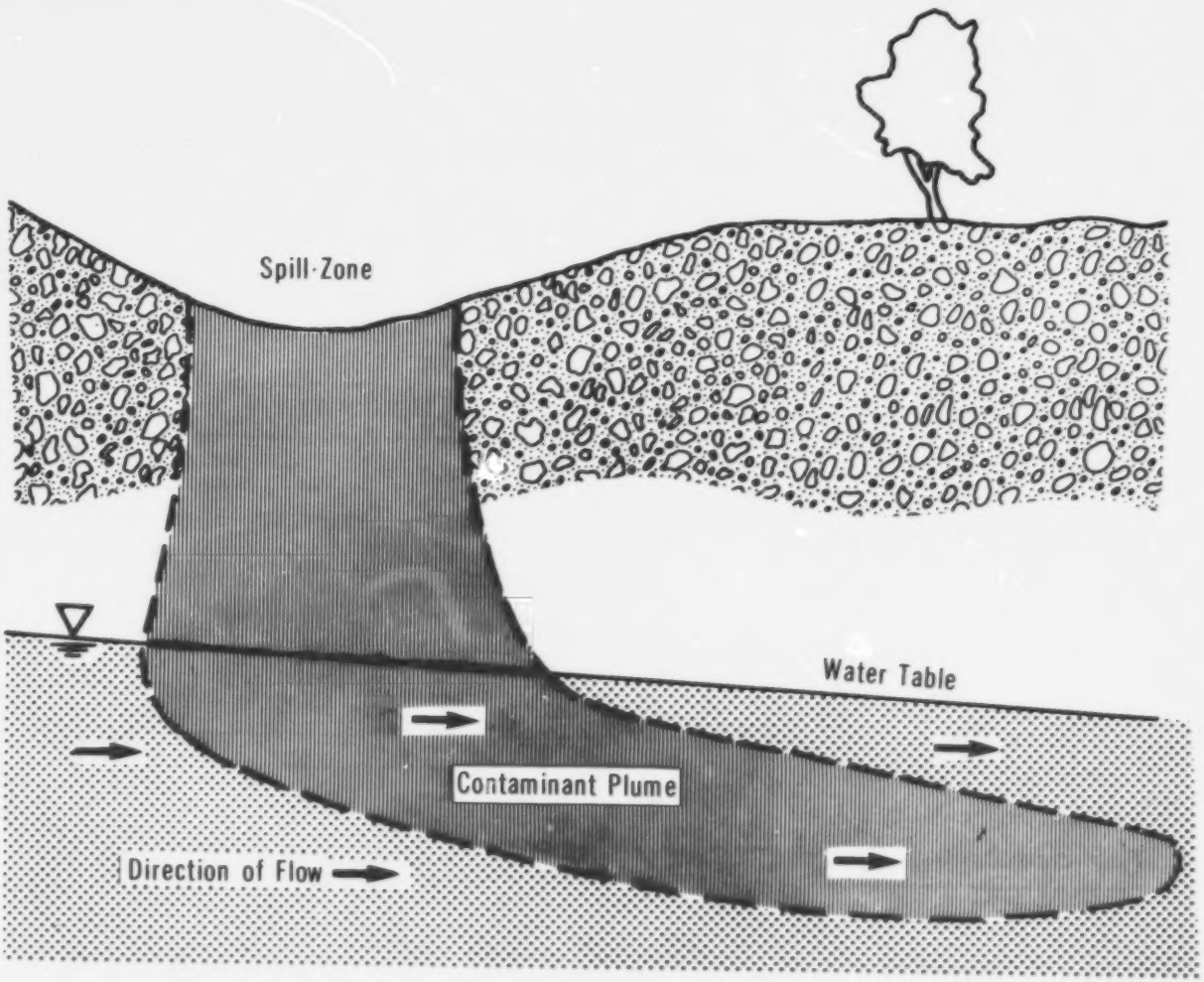
where: k = intrinsic permeability of the soil (m^2)

ρ = mass density of the fluid (kg/m^3)

FIGURE 28

FORMALDEHYDE

SCHEMATIC SOIL TRANSPORT



Soil: Coarse Sand

–Porosity (n) = 0.35

–Intrinsic Permeability (k) = 10^{-9} m^2

–Field Capacity (θ_{fc}) = 0.075

μ = absolute viscosity of the fluid (Pa·s)

g = acceleration due to gravity = 9.81 m/s^2

The fluids involved are 37 percent formaldehyde solution and water. The water calculations represent the extreme as the formaldehyde solution is diluted. The appropriate properties of formaldehyde solution are given in the chart below:

Property	37 Percent Formaldehyde Solution		Water
	20°C	4°C	20°C
Mass density (ρ), kg/m^3	1102	1110	1000
Absolute viscosity (μ), Pa·s	1.9×10^{-3}	3.5×10^{-3}	1.0×10^{-3}
Saturated hydraulic conductivity (K_o), m/s	$(0.57 \times 10^{7})k$	$(0.31 \times 10^{7})k$	$(0.98 \times 10^{7})k$

5.5.4 **Soils.** Three soils are selected for this work. Their relevant properties are:

Property	Soil Type		
	Coarse Sand	Silty Sand	Clay Till
Porosity (n), m^3/m^3	0.35	0.45	0.55
Intrinsic permeability (k), m^2	10^{-9}	10^{-12}	10^{-15}
Field capacity (θ_{fc}), m^3/m^3	0.075	0.3	0.45

5.5.5 **Penetration Nomograms.** Nomograms for the penetration of formaldehyde solution into the unsaturated zone above the groundwater table were prepared for each soil. They present penetration time (t_p) plotted against depth of penetration (B). Because of the methods and assumptions used, the penetration depth should be considered as a maximum depth in time t_p.

A flowchart for the use of the nomograms is presented in Figure 29. The nomograms are presented as Figures 30, 31, and 32. The water line on the nomograms represents the maximum penetration of water at 20°C in time t_p. It is a limiting

FIGURE 29

FORMALDEHYDE

FLOWCHART FOR NOMOGRAM USE

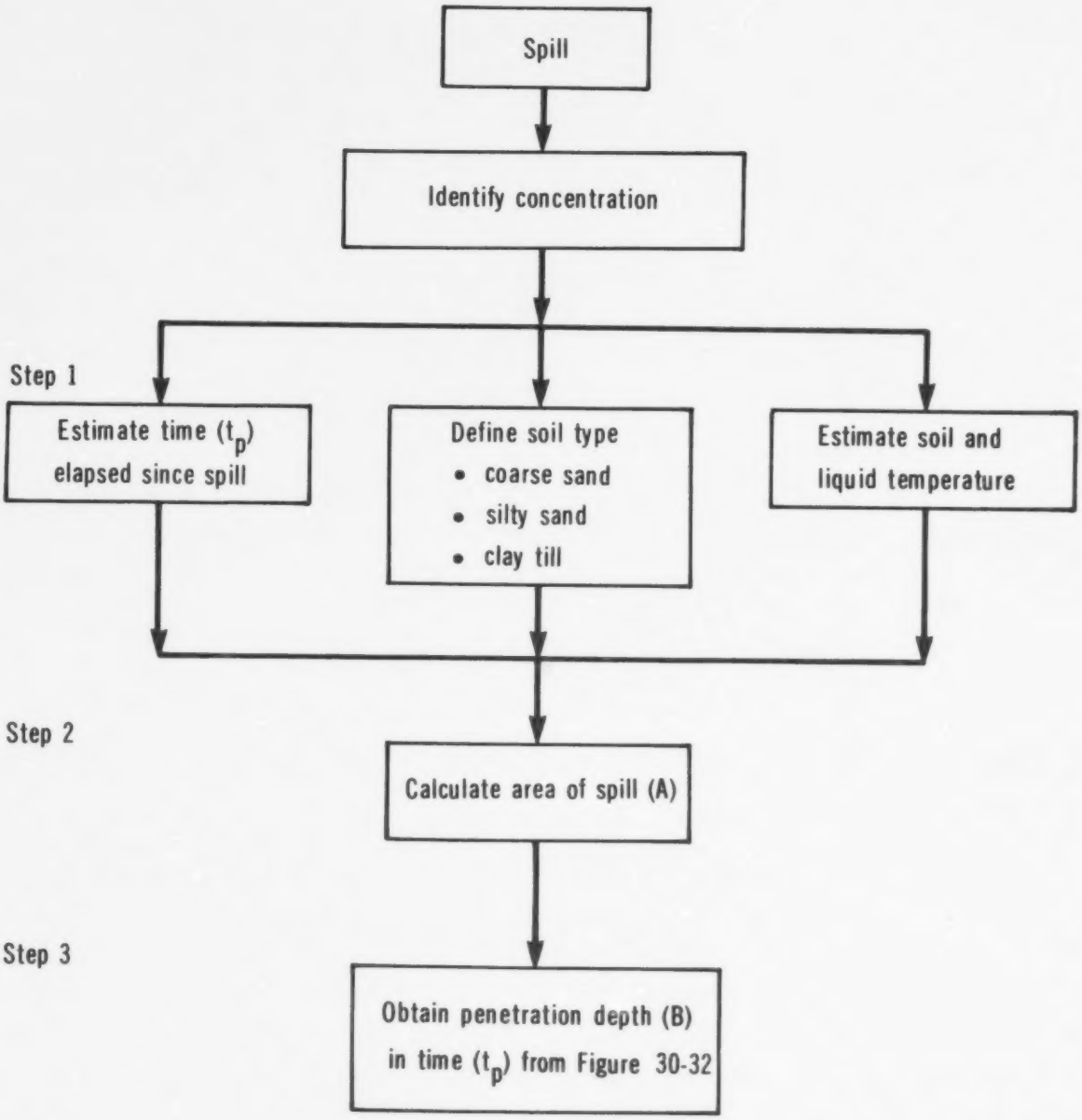


FIGURE 30

FORMALDEHYDE (37% SOLUTION)

PENETRATION IN COARSE SAND

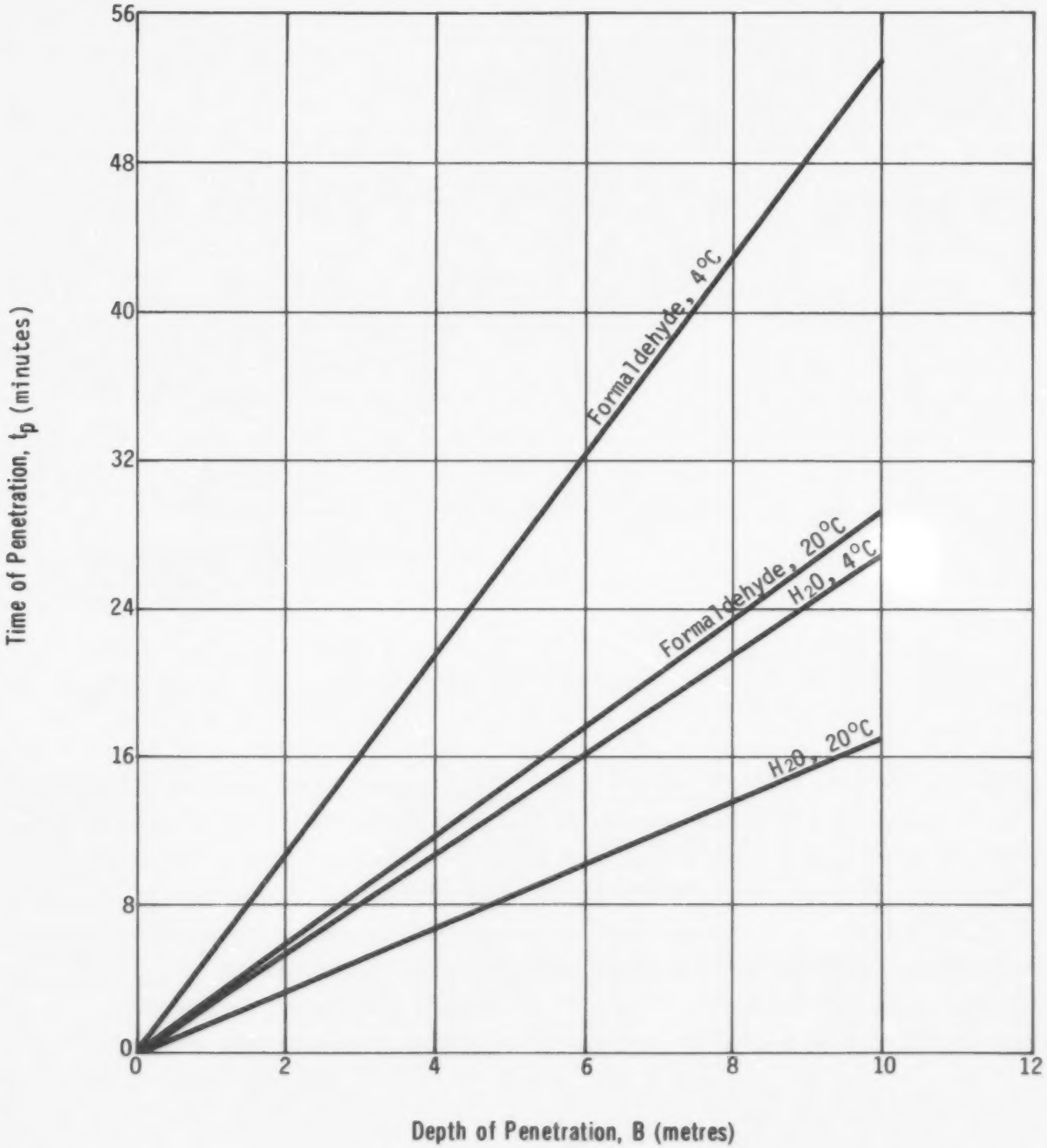


FIGURE 31

FORMALDEHYDE (37% SOLUTION)

PENETRATION IN SILTY SAND

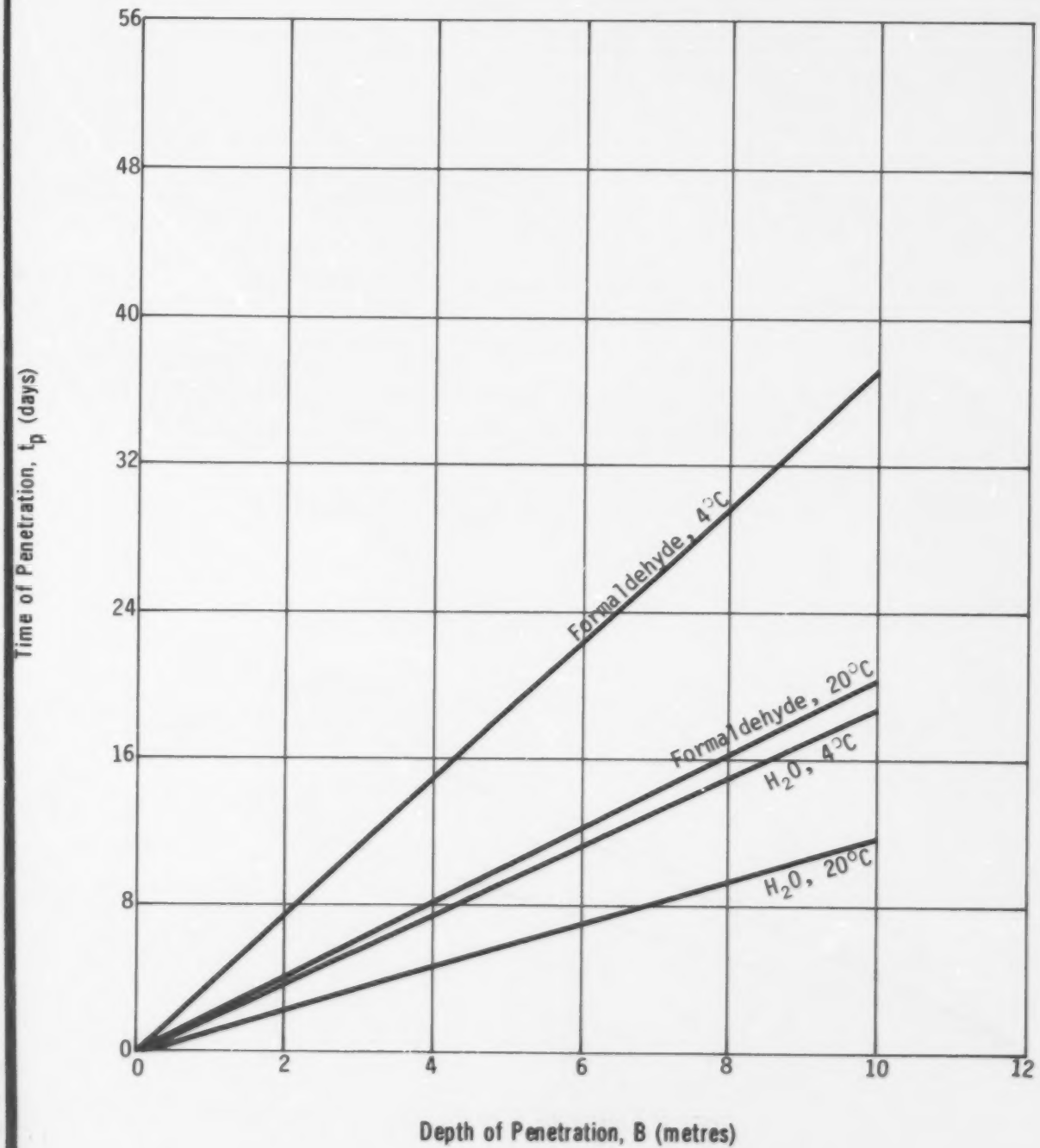
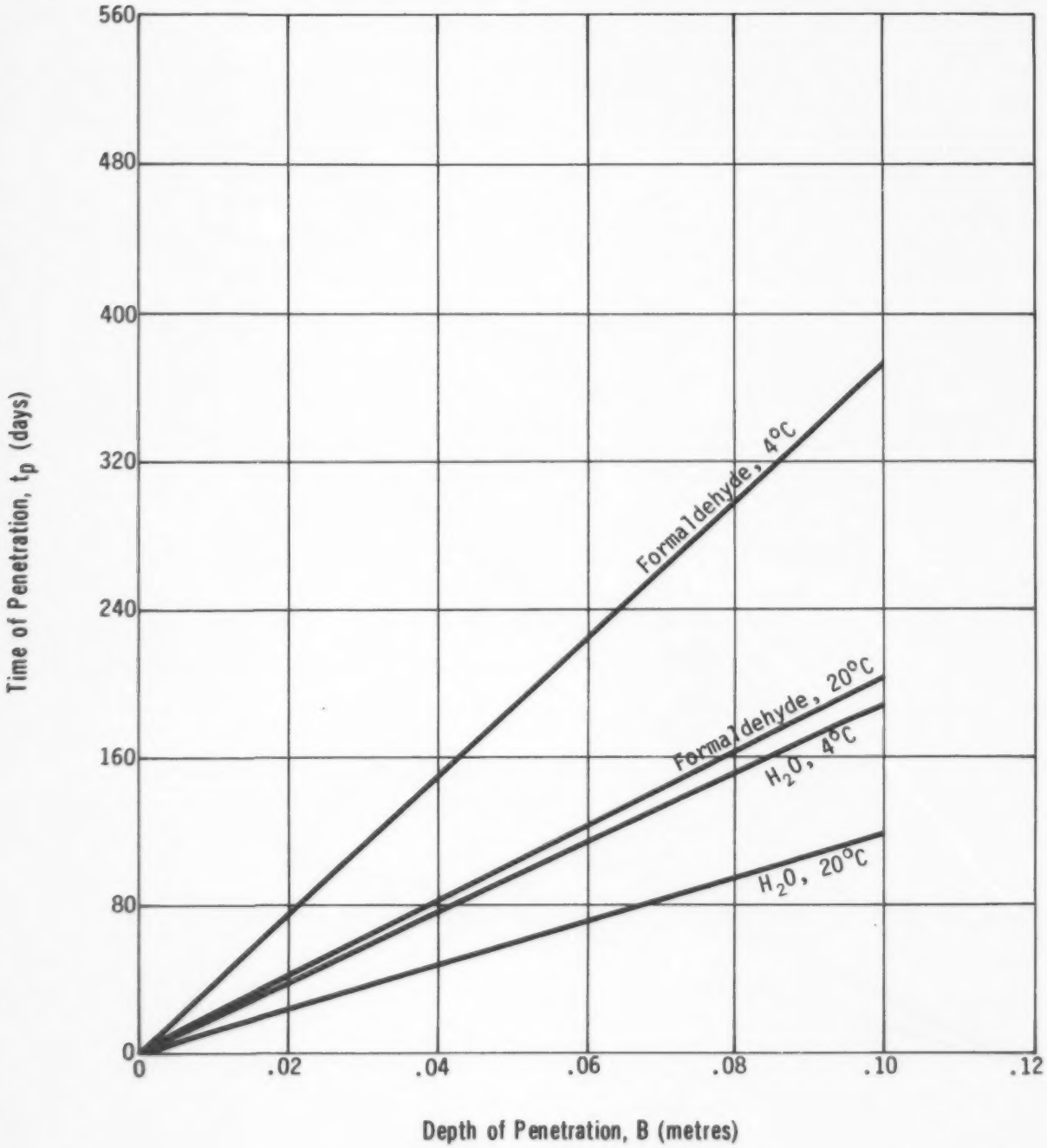


FIGURE 32

FORMALDEHYDE (37% SOLUTION)

PENETRATION IN CLAY TILL



condition as formaldehyde solution becomes diluted with water from precipitation or flushing.

5.5.6 Sample Calculation. A 20 tonne spill of formaldehyde solution has occurred on coarse sand. The temperature is 20°C; the spill radius is 8.6 m. Calculate the depth of penetration 24 minutes after the spill.

Solution

Step 1: Define parameters

- Mass spilled = 20 000 kg (20 tonnes)
- T = 20°C
- r = 8.6 m
- Soil = coarse sand
- Groundwater table depth (d) = 13 m
- Time since spill (t_p) = 24 min

Step 2: Calculate the area of the spill

- $A = \pi r^2 = 232\ m^2$

Step 3: Estimate the depth of penetration (B) at time (t_p)

- For coarse sand, B = 8.2 m at t_p = 24 min
- Groundwater table has not been reached in this time

6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water. None in Canada.

6.1.2 Air. In Canada, the environmental limit for formaldehyde in Ontario is 65 $\mu g/m^3$ of air at the point of human impingement (Ontario E.P. Act 1971). The emission limit for industrial sources is 20 ppm in British Columbia (Law 1982).

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. Formaldehyde has been assigned a TL_m96 of 10 to 100 ppm (RTECS 1979).

6.2.2 Measured Toxicities.

6.2.2.1 Freshwater toxicity.

Conc. (mg/L)	Time (hours)	Species	Result	Conditions	Reference
Fish Kill Data					
100	72	Largemouth bass	lethal	formalin	Helms 1967
100	42	Bluegill	lethal	formalin	Helms 1967
50	24	Trout	died	-	WQC 1963
50	120	Shiners	lethal	18°C	WQC 1963
87	25	Channel catfish fingerlings	lethal	formalin	Clemens 1959
126	48	Channel catfish	lethal	formalin	OHM-TADS 1981
70	72	Carp	lethal	formalin	OHM-TADS 1981
Fish Toxicity Tests					
168	48	Rainbow trout	LC_{50}	static	WQCDB-3 1971
185	48	Brown trout	LC_{50}	static	WQCDB-3 1971
157	48	Brook trout	LC_{50}	static	WQCDB-3 1971
167	48	Lake trout	LC_{50}	static	WQCDB-3 1971
96-126	48	Channel catfish	LC_{50}	static	WQCDB-3 1971
145	48	Bluegill	LC_{50}	static	WQCDB-3 1971
87	24	Channel catfish	LC_{50}	formalin	OHM-TADS 1981
41	96	Zebra fish	LC_{50}	-	JWPCF 1983

Conc. (mg/L)	Time (hours)	Species	Result	Conditions	Reference
15-32.5	48	Golden orfe	LC_{50}	-	JWPCF 1983
100	96	Bluegill	LC_{50}	flow-through	Verschueren 1984
136	96	Smallmouth bass	LC_{50}	flow-through	Verschueren 1984
143	96	Largemouth bass	LC_{50}	flow-through	Verschueren 1984
565-700 (37%)	96	Rainbow trout - green egg stage	LC_{50}	static	Verschueren 1984
198-435 (37%)	96	Rainbow trout - eyed egg stage	LC_{50}	static	Verschueren 1984
89.5-112 (37%)	96	Rainbow trout - SAL larval stage	LC_{50}	static	Verschueren 1984
62-145 (37%)	96	Rainbow trout - fingerlings	LC_{50}	static	Verschueren 1984
440-618 (37%)	96	Rainbow trout	LC_{50}	static	Verschueren 1984
118	96	Rainbow trout	LC_{50}	flow-through	Verschueren 1984
100	96	Lake trout	LC_{50}	flow-through	Verschueren 1984
62	96	Black bullhead	LC_{50}	flow-through	Verschueren 1984
66	96	Channel catfish	LC_{50}	flow-through	Verschueren 1984
173	96	Green sunfish	LC_{50}	flow-through	Verschueren 1984
224 (37%)	96	American eel - black eel stage	LC_{50}	22°C, static, pH 7.2-7.6, HD 40-48	JWPCF 1981
84 (37%)	96	American eel - glass eel stage	LC_{50}	22°C, static, pH 7.2-7.6, HD 40-48	JWPCF 1981
330 (37%)	96	American eel - yellow phase	LC_{50}	22°C, static, pH 7.2-7.6, HD 40-48	JWPCF 1981
3.7-11.1	24	Striped bass fingerlings	LC_{50}	static	NRC 1981
10	48 to 96	Striped bass larvae	LC_{50}	static	Hughes 1973
15	24	Striped bass larvae	LC_{50}	static	OHM-TADS 1981
15	48 to 96	Striped bass fingerlings	LC_{50}	static	Hughes 1973

Conc. (mg/L)	Time (hours)	Species	Result	Conditions	Reference
35	24	Striped bass fingerlings	LC_{50}	static	Hughes 1973
50	48	Brown trout	TL_m	18-20°C, hard: static and flow-through	Middlebrooks 1973
76	24	Brown trout	TL_m	18-20°C, hard: static and flow-through	Middlebrooks 1973
50	48	Rainbow trout	TL_m	18-20°C, hard; static and flow-through	Middlebrooks 1973
76	24	Rainbow trout	TL_m	18-20°C, hard; static and flow-through	Middlebrooks 1973
100	48	Trout	TL_m	temperature controlled	Wilford 1966
25	48 to 96	Catfish	TL_m	-	WQC 1963
32	24	Catfish	TL_m	-	OHM-TADS 1981
Invertebrates					
37	72	Crayfish (*Procambarus blandingi*)	No effect	-	NRC 1981
5	tns	*Daphnia magna*	LC_{100}	-	NRC 1981
2	48	Daphnia	TL_m	23°C	WQC 1963
Other Species					
100-120	48	Bull frog tadpoles	LC_{30}	-	NRC 1981
15	72	Bull frog tadpoles	LC_{100}	-	NRC 1981
11-18.5	72	Leopard frog tadpoles (*Rana pipiens*)	LC_{100}	-	NRC 1981
37	72	Salamander larvae (*Amblystoma tigrinum*)	not toxic	-	NRC 1981

Conc. (mg/L)	Time (hours)	Species	Result	Conditions	Reference
Microorganisms					
3	96	Algae (*Scenedesmus obliquus*)	TL_m	24°C	NRC 1981
74	tns	Aerobic water organisms	50% inhibition of oxygen utilization	-	NRC 1981
130-170	tns	Aerobic water organisms	toxic threshold	-	NRC 1981
37	168	Aquatic algae (*Aphanothece*, *Oscillatoria* and *Raizoclonium* species)	no effect	-	NRC 1981
5.6	168	Aquatic algae (*Scenedesmus*, *Sirogonium*, *Spyrogyra* and *Stigeoclonium* species)	LC_{100}	-	NRC 1981
1	tns	Bacteria (*E. coli*)	toxic	-	Verschueren 1984
0.3-0.5	tns	Algae (*Scenedesmus*)	toxic	-	Verschueren 1984
5	tns	*Microregma*	TL_m	-	OHM-TADS 1981
14	tns	Bacteria (*Pseudomonas putida*)	inhibition of cell multiplication	-	Verschueren 1984
0.39	tns	Algae (*Microcystis aeruginosa*)	inhibition of cell multiplication	-	Verschueren 1984
2.5	tns	Green algae (*Scenedesmus quadricauda*)	inhibition of cell multiplication	-	Verschueren 1984
22	tns	Protozoa (*Entosiphon sulcatum*)	inhibition of cell multiplication	-	Verschueren 1984
6.5	tns	Protozoa (*Uronema parduczi*)	inhibition of cell multiplication	-	Verschueren 1984

6.2.2.2 Saltwater toxicity.

Conc. (mg/L)	Time (hours)	Species	Result	Conditions	Reference
69.1-74.9	96	*Trachinotus carolinas* (juvenile)	LC_{50}	static, formalin	OHM-TADS 1981
18	96	Striped bass fingerlings	LC_{50}	saltwater, static	OHM-TADS 1981
100-300	48	Flounder	LC_{50}	saltwater, aerated	Portman 1970
173 (37%)	96	Atlantic salmon	LC_{50}	flow-through	Verschueren 1984
330-1000	48	Shrimp (*Crangon crangon*)	LC_{50}	continuous aeration	WQCDB 1973

6.3 Avian Toxicity

Egg fertility decreased in geese raised on sites contaminated with formaldehyde. Adult geese showed no signs of disease (Jopek 1980).

6.4 Toxicity to Plants

Numerous tests on plant species reveal that low levels of formaldehyde do not apparently harm plants. Toxic levels have not been defined for any species. A number of study summaries follow (NRC 1981). Spinach, endive, beet, oats and alfalfa showed no injuries at 2 ppm for 2 hours. At 0.7 ppm for 5 hours, alfalfa showed mild atypical injury signs. In another study, pinto beans were treated with 1.6-16.0 ppm formaldehyde treated with UV light. Injury was not observed. Formaldehyde was mixed with nitrogen oxides, treated with UV light and admitted to pinto beans, tobacco and petunias; levels of 5.6 and 6.1 ppm did not damage plants. Other studies have noted that algae (*Euglena gracilis*), kidney beans and barley were not affected at levels below 0.08 ppm.

Pollen germination under formaldehyde exposures was also examined. A 1- or 2-hour exposure to 0.37 ppm did not affect pollen; however, a 5-hour exposure reduced the pollen tube length. A 1-hour, 2.4 ppm dose also reduced pollen tube length. Seedling growth in two separate incidents was affected by what was suspected to be formaldehyde released from the seedling boxes. Paraformaldehyde pills are used on sugar maple trees to increase or prolong the yield of sap. Preliminary investigation revealed that the formaldehyde altered the vascular and ray systems of the trees on a long-term basis.

6.5 Effect Studies

A level of 95 ppm formaldehyde has been found to cause tainting of fish flesh (WQC 1972). Formaldehyde acts as a protoplasmic poison, largely because it coagulates protein (MHSSW 1976; EPA 560/2-76-009).

6.6 Degradation

B.O.D. kg/kg	B.O.D. % Theor.	Days	Seed	Method	Reference
0.6-1.07	60%	5	Sewage seed	-	Verschueren 1984
0.3-1.06		5	Sewage seed		Henkelekian 1971
1.06	100			C.O.C.	Jones 1971
<1	47	5	Activated sludge	quiescent	Ryerman 1966
>1	99	5	Activated sludge	quiescent	Ryerman 1966
<1	0	5	Pure bacteria culture		Ryerman 1966
1.228	-	20	-	-	Verschueren 1984

Formaldehyde concentrations of 50-720 mg/L resulted in lag periods of more than 2 days before oxidation began. After acclimatization, 95 percent removal was achieved (1750 mg/L initial concentration). Buffering with sodium bicarbonate reduced inhibition (EPA 660/2-77-239). Inhibition of sludge digestion begins at 100 mg/L (Verschueren 1984). Inhibition of the degradation of glucose by bacteria begins at 1-2 mg/L (Verschueren 1984).

6.7 Ambient Levels

Formaldehyde is a fairly ubiquitous chemical in nature at relatively low levels (<4 ppb). It is found in many fruits (e.g., pineapple, apple) and is emitted by many plants, both at low levels. It is produced by many combustion reactions such as in engines, and burning of garbage, wood, tobacco, etc. It is emitted from many building materials especially wood and particle board since urea-formaldehyde resin is used as a glue. The typical levels of formaldehyde in an urban atmosphere are 4-150 ppb. In occupational environments, this can be much higher, e.g., 0.04-14 ppm in plywood or laminates plants, 0.09-6 ppm in funeral homes and 0.9-3.3 ppm in textile plants, garment factories and clothing stores (NRC 1981).

6.8 Long-term Fate

The half-life of formaldehyde in the lower atmosphere is calculated to be 2.6 hours; the processes are complex and the pathways are difficult to define. Formaldehyde ultimately "comes down" and the "wash out" of atmospheric formaldehyde to the sea has been estimated at 1-6 $\mu g/cm^2$ sea surface per year in various studies. Washout rates over land are estimated to be greater and contribute largely to the removal of atmospheric formaldehyde (NRC 1981).

Bioaccumulation and concentration effects have not been found (Sills 1979).

7 HUMAN HEALTH

The irritant effects of formaldehyde are well known. Eye and skin irritation resulting from exposure to this chemical have been described in the literature for both human and test animals. In addition, reports of symptoms from inhalation exposures range from irritation due to moderate exposures, to pulmonary edema and death as a result of severe exposures.

Its health effects have been widely documented recently due to the publication of two complementary animal studies relating formaldehyde exposure to cancer (NIOSH 1980). Formaldehyde has also been shown to be a mutagen in several short-term laboratory studies (NIOSH 1980). No conclusive information was found concerning the teratogenic effects of the compound. A 1976 Criteria Document (NIOSH 1976) and the USA-ACGIH TLV® Documentation (Doc. TLV 1981) concentrated on the eye and respiratory tract irritation effects of formaldehyde and its potential as a sensitizing agent. In 1980, NIOSH issued Current Intelligence Bulletin No. 34, Formaldehyde: Evidence of Carcinogenicity (NIOSH 1980). While the OSHA standard remains unaltered to date, the Bulletin recommends that formaldehyde be handled in the workplace as a potential occupational carcinogen.

In Canada, the use of urea formaldehyde foam insulation was found to release formaldehyde into homes. As a result, further use of the foam as an insulating material has been banned.

The toxicological data summarized here have been extracted from reliable standard reference sources. It should be noted that some of the data are for chronic (long-term) low-level exposures and may not be directly applicable to spill situations. With the exception of data pertaining to mutagenicity, teratogenicity and carcinogenicity, only acute (short-term) exposure data are given for nonhuman mammalian species, to support interpretation of the human data where appropriate.

7.1 Recommended Exposure Limits

The exposure standards for formaldehyde are based upon its irritant properties and lung effects, with the consideration that exposed workers become acclimatized to formaldehyde exposure and can tolerate increased levels without showing adverse effects. Canadian provincial guidelines generally are similar to those of the USA-ACGIH, unless indicated otherwise.

Guideline (Time)	Origin	Recommended Level	Reference
Time-weighted Averages (TWA)			
TLV●	USA-ACGIH	1 ppm (1.5 mg/m^3)	TLV 1983
PEL (8 h)	USA-OSHA	3 ppm	NIOSH/OSHA 1981
Occupational Standard	Canada Labour Code	2 ppm	Tataryn 1983
Indoor Ambient Level	Proposed - USA, HUD	0.4 ppm	EST 1984
Short-term Exposure Limits (STEL)			
STEL	USA-ACGIH	2 ppm (3 mg/m^3)	TLV 1983
Ceiling (30 min)	USA-NIOSH	1 ppm	NIOSH/OSHA 1981
Other Human Toxicities			
IDLH	USA-NIOSH/ OSHA	100 ppm	NIOSH Guide 1978
TC_{LO}	-	17 mg/m^3	RTECS 1979
LD_{LO}	-	477 mg/kg	RTECS 1979
LD_{LO} (woman)	-	36 mg/kg	RTECS 1979

Inhalation Toxicity Index

The Inhalation Toxicity Index (ITI) is a measure of the potential of a substance to cause injury by inhalation. It is calculated as follows:

ITI = 1315.12 (Vapour Pressure, in mm Hg/TLV●, in ppm)

At -19°C, ITI = 1315.12 (757.56 mm Hg/2 ppm)

At -19°C, ITI = 5×10^5

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
10.5 to 41.7 ppm (10 min)	Bilateral vesicle reaction on hands of hypersensitive person.	Horsfall 1934. IN NIOSH 1976
16 to 30 ppm (8 h/d)	Among 60 exposed individuals, skin reactions were reported; 16 workers had dermatitis, with marked erythema of neck and face.	Glass 1961. IN NIOSH 1976
2 percent solution	Irritant threshold for solutions.	Law 1982
Various (chronic exposure	Primary irritation of exposed skin in direct contact with liquid and gas.	Pirila and Kilpio 1949; Roth 1969. IN NIOSH 1976
Various (chronic exposure	Allergic dermatitis by direct skin contact with formaldehyde solutions.	O'Quinn and Kennedy 1965; Berrens et al. 1964; Peek and Palitz 1956; Fisher et al. 1962; Shellow and Altman 1966; Marcussen 1962; Skogh 1959. IN NIOSH 1976
Various (chronic exposure	Allergic dermatitis from skin contact with formaldehyde containing resins.	Ettinger and Jeremias 1955; Pirila and Kilpio 1949; Keil and Van Dyck 1944; Logan and Perry 1973; Frank 1964. IN NIOSH 1976
Various (chronic exposure	Allergic dermatitis from exposure to gaseous formaldehyde.	Kratochuil 1971; Hovding 1969; Glass 1961; Pirila and Kilpio 1949; Horsfall 1934; Harris 1953. IN NIOSH 1976
SPECIES: Rabbit		
540 mg/kg	Mild irritation, open skin.	RTECS 1979
50 mg/kg	Moderate irritation.	RTECS 1979
0.1 to 20 percent solution	Mild irritation.	NRC 1981

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
16 to 30 ppm (8 h/d, chronic)	Eye irritation.	Glass 1961. IN NIOSH 1976.
13.8 ppm (30 min)	Eye irritation subsided after 10 minutes in the chamber.	Sim and Pattle 1957. IN NIOSH 1976
0.09 to 5.26 ppm (with paraformaldehyde)	Eye irritation.	Kerfoot and Mooney 1975. IN NIOSH 1976
4 ppm (5 min)	Irritation.	RTECS 1979
0.9 to 3.3 ppm	Mild irritation.	Miller and Blejer 1966. IN NIOSH 1976
0.9 to 2.7 ppm	Tearing. Greatest effect at the beginning of the workday and after lunch period.	Blejer and Miller 1966. IN NIOSH 1976
0.9 to 1.6 ppm (8 h/d)	Itching eyes.	Morrill 1961. IN NIOSH 1976
1.4 ppm	Eye sensitivity to light lowered in unacclimatized population.	Melekhina 1964. IN NIOSH 1976
0.07 to 1.3 ppm (10 min)	Optical chronaxy changes in unacclimatized individuals.	Melekhina 1964. IN NIOSH 1976
0.3 to 0.5 ppm (5 min)	In a smog chamber, increased blink rate in proportion to formaldehyde concentration.	Schuck et al. 1966. IN NIOSH 1976
0.25 to 1 ppm	Irritation threshold.	EST 1984
0.01 ppm	Lower threshold for burning sensation and tearing.	Tataryn 1982
SPECIES: Cat		
8150 ppm (3.5 h)	Bloody discoloration of aqueous humor.	TDB (on-line) 1981
4900 ppm (3 h)	Necrotic lesions in corneas.	TDB (on-line) 1981
SPECIES: Rabbit		
40 to 70 ppm	Slight irritation.	NRC 1981
750 µg/kg	Severe irritation.	RTECS 1979
0.005 mL of 15 percent formalin	Severe reaction, corneal and conjunctival edema.	NRC 1981

7.3 Threshold Perception Properties

7.3.1 Odour.

Odour Characteristics: Hay, straw-like; hedonic tone; pungent (Verschueren 1984).

Odour Index: 5 000 000 at 20°C (Verschueren 1984).

Parameter	Media	Concentration	Reference
Recognition Threshold	in air	1.00 ppm	ASTM 1980
Odour Detection Limit	in air	4.99 ppm	ASTM 1980
Odour Detection Limit	in air	2.50 ppm	ASTM 1980
Low Odour Threshold	in air	0.05 to 1.00 ppm	NRC 1981

7.3.2 Taste Threshold.

Parameter	Media	Concentration	Reference
Lower Taste Threshold	in water	20 to 50 ppm	Kirk-Othmer 1980
Odour Threshold Range	in water	0.8 to 102 ppm	Verschueren 1984

7.4 Toxicity Studies

7.4.1 Inhalation.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
100 ppm and above	Severe toxic effects and possibly death.	NRC 1981
50 to 100 ppm	Pulmonary edema, inflammation, pneumonia.	NRC 1981
10 to 20 ppm	Severe coughing.	Tataryn 1983

Exposure Level (and Duration)	Effects	Reference
0.09 to 5.26 ppm	Formaldehyde with paraformaldehyde. Eye and upper respiratory irritation; lessened during the day, returned after lunch and next day.	Kerfoot and Mooney 1975. IN NIOSH 1976
4 to 5 ppm	Toleration threshold.	Law 1982
0.9 to 2.7 ppm	Tearing of eyes and irritation of nasal passages and throat. Irritant effects were greatest at the beginning of exposure.	Blejer and Miller 1966. IN NIOSH 1976
0.8 to 1 ppm	Threshold for bronchitis and asthma.	EST 1984
0.053 mg/m^3	Changes in cerebral electrical activity.	Fel'dman and Bonashevskaya 1971. IN NIOSH 1976
0.04 mg/m^3	No alteration of cerebral electrical activity in subjects.	Fel'dman and Bonashevskaya 1971. IN NIOSH 1976
SPECIES: Cat		
820 mg/m^3 (8 h)	LC_{LO}	RTECS 1979
SPECIES: Rat		
815 (3 min)	LC_{50}	NRC 1981
479 ppm (4 h)	LC_{50}	NRC 1981
250 ppm (4 h)	LC_{LO}	RTECS 1979
> 0.3 ppm (1 h)	Increased pulmonary flow resistance not statistically significant until 10 ppm or greater.	TDB (on-line) 1981
SPECIES: Mouse		
900 mg/kg (2 h)	LD_{LO}	TDB (on-line) 1981
Chronic Exposures		
SPECIES: Human		
1 to 11 ppm (8 h/d)	Eye, nose and throat irritation.	Stickney 1958. IN NIOSH 1976

Exposure Level (and Duration)	Effects	Reference
0.9 to 1.6 ppm (8 h/d)	Itching eyes, dry sore throat, disturbed sleep, and unusual thirst upon waking in the morning.	Morrill 1961. IN NIOSH 1976
0.8 ppm (daily)	Equilibrium and olfactory sensation shifts, irritation of upper respiratory tract and eyes in most sensitive individuals, enhancement of alpha-rhythms.	Zaeva et al. 1968. IN NIOSH 1976
SPECIES: Rat		
1.6, 4.6 or 8.1 ppm (45-90 d)	At 1.6 ppm, slight discoloration of hair. At 4.6 ppm (45 d), weight loss. At 8.1 ppm (60 d), respiratory and eye irritation, weight loss.	NRC 1981
4, 12.7 or 38.1 ppm (6 h/d, 50 d/wk, 113 wk)	No adverse effects at 4 ppm. At 12.7 ppm, weight loss and nasal irritation. At 38.1 ppm, ulceration and necrosis of nasal mucosa.	NRC 1981

7.4.2 Ingestion.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
240 mL, 37 percent solution	Severe pain, ulceration and stenosis of stomach, dysphagia.	Roy et al. 1962. IN NIOSH 1976
120 cm^3, 10 percent solution	Gastric shrinkage after 3 months.	Bartone et al. 1968. IN NIOSH 1976
100 cm^3 (unspecified concentration)	Severe epigastric pain, passed black stool; dysphagia, stenosis and corrosive destruction of the stomach.	Heffernon and Hajjar 1964. IN NIOSH 1976
4 oz. (formalin)	Cyanosis, low temperature, shallow respiration, weak, rapid and irregular pulse.	Earp 1916. IN NIOSH 1976

Exposure Level (and Duration)	Effects	Reference
1.5 oz. (formalin)	Cyanosis, vomiting, dry mucous membranes in mouth and throat, weak and irregular pulse, shallow respiration.	Earp 1916. IN NIOSH 1976
0.5 oz., 37 to 40 percent solution	Coma, recovery with treatment.	Bower 1909. IN NIOSH 1976
36 mg/kg	Woman, LD_{LO}	RTECS 1979
SPECIES: Guinea Pig		
260 mg/kg	LD_{50}	DPIMR 1981
SPECIES: Rat		
800 mg/kg	LD_{50}	RTECS 1979
Chronic Exposures		
SPECIES: Human		
100 mg/d, for 5 d, then 200 mg/d for 10 d	Given in milk. Headache, stomach pain, burning sensation in throat, rash on chest and thighs in 4 out of 11 cases.	Wiley 1908. IN NIOSH 1976
22 to 200 mg (daily for 13 wk)	Mild gastric and pharyngeal discomfort.	Yonkman et al. 1941. IN NIOSH 1976

7.4.3 Subcutaneous.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Dog		
550 mg/kg	LD_{LO}	DPIMR 1981
SPECIES: Rat		
420 mg/kg	LD_{50}	DPIMR 1981
SPECIES: Mouse		
300 mg/kg	LD_{50}	RTECS 1979

7.4.4 Mutagenicity, Teratogenicity and Carcinogenicity.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rabbit		
Unspecified	Lung bronchial cell hyperplasia with hypermucigenesis.	TDB (on-line) 1981
SPECIES: Rat		
15 ppm (6 h/d, 5 d/wk, 16 mo)	Some developed cancer by the 12th month. Squamous cell nasal carcinoma originating in epithelium of nasal turbanates.	CIIT 1979. IN NIOSH 1980
10.6 to 14.6 ppm (6 h/d over a period of 814 d) (with HCl)	25 out of 100 male rats developed squamous cell carcinoma and 2 developed benign papillomas.	Nyu 1979. IN NIOSH 1980
6 ppm (6 h/d, 5 d/wk for 16 mo)	One case of squamous cell carcinoma originating from layer of skin in nose.	CIIT 1979. IN NIOSH 1980
0.3 to 15 ppm (6 h)	Evidence that DNA-protein cross-linking forms in respiratory mucosa at concentrations greater than 2 ppm, no bonding to bone macromolecules was observed.	CIIT 1984a
14.3 ppm (up to 2 yr)	50 percent incidence of nasal cavity squamous cell carcinomas.	CIIT 1984b
200 to 900 mg/m^3 (variable durations)	No evidence of lung cancer.	Horton et al. 1963. IN NIOSH 1976
0.012 to 1 mg/m^3 (10 to 15 d)	Exposed 10 to 15 days before impregnation and during pregnancy. Total body weights and weights of some organs were increased in offspring of exposed. Lung and liver weights were lower than in offspring of controls.	Gofmekler 1966. IN NIOSH 1976
SPECIES: Mouse		
6 to 15 ppm (6 h/d, 5 d/wk, 16 mo)	Mice developed nasal squamous cell carcinoma.	CIIT 1979. IN NIOSH 1980

Exposure Level (and Duration)	Effects	Reference
SPECIES: Nonmammalian		
Various	Positive mutagenic effects have been reported in fruit flies (Drosophila), grasshopper, flowering plants, fungi and bacteria.	Auerback and Moutschen 1977. IN NIOSH 1980; ECETOC 1981; NRC 1981
SPECIES: *Salmonella typhimurium*		
Various	Positive mutagenicity results in severe Ames tests.	EST 1984

7.5 Symptoms of Exposure

General symptoms of exposure found in most information sources have not been specifically referenced. Only those of a more specific or unusual nature have their sources indicated.

7.5.1 Inhalation.

1. Irritation.
2. Coughing.
3. Tightening of the chest (NIOSH 1980).
4. Tearing.
5. Eye irritation.
6. Altered functional state of the cerebral cortex (NIOSH 1976).
7. Equilibrium and olfactory sensation shift.
8. Prickling and itching of mucous membranes.
9. Enhancement of alpha-rhythms (NIOSH 1976).
10. Heart palpitations.
11. Disturbed sleep.
12. Unusual thirst.
13. Sore throat.
14. Nausea (CHRIS 1978).
15. Vomiting (CHRIS 1978).

16. Bronchitis.
17. Dysphagia (TDB (on-line) 1981).
18. Gastric pain (NIOSH 1976).
19. Pneumonitis.
20. Hemorrhage (AAR 1981).
21. Death.

7.5.2 Ingestion.

1. Passage of black stool (NIOSH 1976).
2. Epigastric pain.
3. Vomiting.
4. Low temperature.
5. Shallow respiration.
6. Weak, rapid and irregular pulse.
7. Dry mucous membranes and inflammation (AAR 1981).
8. Destruction of the stomach (NIOSH 1976).
9. Stenosis.
10. Ulceration of the stomach.
11. Cyanosis.
12. Dysphagia (TDB (on-line) 1981).
13. Gastric shrinkage (NIOSH 1976).
14. Coma.
15. Death.

7.5.3 Skin Contact.

1. Irritation.
2. Bilateral vesicle reactions.
3. Tanning effect (AAR 1981).
4. Allergic sensitization.

7.5.4 Eye Contact.

1. Lacrimation.
2. Irritation.
3. Itching.
4. Lowering of eye sensitivity to light.
5. Optical chronaxy.

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Formaldehyde with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION VESSELS	SOLUBILIZATION IN CLOSED	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
GENERAL														
Fire		•	•			•							Irritant gaseous formaldehyde may be evolved in a fire. Formaldehyde solutions will burn and/or possibly explode if heated above their flash points.	Sax 1979
Heat		•	•			•							Gas is vaporized readily from solution and is flammable in air.	Sax 1979; NFPA 1978
SPECIFIC CHEMICALS														
Hydrogen Peroxide			•											Bretherick 1979
Magnesium Carbonate			•					•					Explosion due to pressure of CO_2 from reaction.	Bretherick 1979

8.1 Compatibility of Formaldehyde with Other Chemicals and Chemical Groups
(Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Nitric Acid									•				Violent reaction causes decomposition to CO_2 and H_2O.	Walker 1964
Nitrogen Dioxide			•										Explosive at 180°C.	NFPA 1978
Nitromethane			•										Introduction of air will cause flash explosion or violent fumes.	Bretherick 1979
Performic Acid (Peroxyformic Acid)			•							•			Formaldehyde is oxidized violently by concentrated performic acid and the mixture can explode violently.	NFPA 1978; Bretherick 1979
Phenol							•						Possible explosion.	Bretherick 1979
CHEMICAL GROUPS														
Alkali and Alkaline Earth Metals	•		•										Generation of flammable hydrogen gas may result.	EPA 600/2-80-076

8.1 Compatibility of Formaldehyde with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Amines	•												Exothermic condensation to form amines.	EPA 600/2-80-076
Azo Compounds	•												Exothermic reaction giving off nitrogen gas.	EPA 600/2-80-076
Caustics	•			•									Self-condensation.	EPA 600/2-80-076
Dithiocarbamates			•			•							Toxic and flammable carbon disulphide may result.	EPA 600/2-80-076
Epoxides											•			EPA 600/2-80-076
Nitrides	•			•	•								Condensation reactions - flammable ammonia gas may result.	EPA 600/2-80-076
Nitro Compounds	•												Condensation reactions.	EPA 600/2-80-076

8.1 Compatibility of Formaldehyde with Other Chemicals and Chemical Groups
(Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Organic Peroxides	•									•			Violent reaction with peroxy acids. Reaction products are unstable to heat and shock.	EPA 600/2-80-076
Oxidizing Agents	•	•			•								Formation of corresponding carboxylic acid may also occur.	EPA 600/2-80-076
Reducing Agents	•		•										Flammable hydrogen gas can be generated.	EPA 600/2-80-076
Sulphides	•												Gemhydroxythiols are produced.	EPA 600/2-80-076
Unsaturated Aliphatics	•												A Diels-Alder type exothermic reaction may take place.	EPA 600/2-80-076

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following procedures have been derived from a literature review. To avoid any deviation from the intended meaning, the wording of the original source has been presented essentially unchanged - in so doing, it is recognized that there may be discrepancies between different sources of information. It is recognized that countermeasures are dependent on the situation, and thus what may appear to be conflicting information may in fact be correct for different situations. The following procedures should not be considered as Environment Canada's recommendations.

9.1.1 Fire Concerns. Formaldehyde is a combustible liquid (GE 1977). The gas vaporizes readily from solution and is flammable in air (NFPA 1978). The vapours may spread away from the spill and ignite. Containers may explode in heat of fire (ERG 1980). Oxygen from the air can oxidize formaldehyde to corrosive formic acid, especially when heated (GE 1977).

9.1.2 Fire Extinguishing Agents. Use water spray to cool containers involved in a fire to prevent rupture (ERG 1980; NFPA 1978).

Small fires: Dry chemical, CO_2, water spray or foam (alcohol).
Large fires: Water spray, fog or foam.

Move containers away from fire area if this can be done without risk. Stay away from tank ends. Do not get water inside containers (ERG 1980). In extinguishing fires with water, use copious amounts (Law 1982).

9.1.3 Spill Actions.

9.1.3.1 General. Stop or reduce discharge of material if this can be done without risk. Eliminate all sources of ignition. Avoid skin contact and inhalation (Celanese MSDS 1979). Use water spray to diminish vapours and to protect men attempting to stop the leak (NFPA 1978). Application of a fluorocarbon water foam to diminish vapours and fire hazard during spills is also recommended (EPA 670/2-75-042). Cellosize and Hycar are absorbent materials which have shown possible applicability for vapour suppression and/or containment of formaldehyde spills (ICI 1982). Leaking containers should be removed to a safe place for repairs and the contents transferred to a sound container (MCA 1960).

9.1.3.2 Spills on land. Contain if possible by forming mechanical barriers to prevent spreading. Neutralize the contained material with lime or sodium bicarbonate (EPA 670/2-75-042). Neutralization with ammonium hydroxide or complexation with sodium sulphite is also recommended as in situ treatment agents (Celanese MSDS 1979).

9.1.3.3 Spills in water. Contain if possible by using natural barriers. Remove trapped material with suction hoses (EPA 670/2-75-042).

9.1.4 Cleanup and Treatment.

9.1.4.1 Spills on land. The remaining contaminated area may be finally washed with diluted ammonia solution to eliminate any vapours (Celanese MSDS 1979). The preferential washing agent is a 1 percent sodium bicarbonate solution (CCPA 1983).

9.1.4.2 Spills in water. Lime and sodium bicarbonate can also be used as neutralizing agents (EPA 670/2-75-042).

9.1.4.3 General. Treatment by trickling filters removes 15-28 percent (feed 110-360 ppm), activated sludge removes 47-94 percent in 5 days (feed 370-1500 ppm), and activated charcoal removes 9 percent (1000 mg/L feed) (Verschueren 1984).

Reverse osmosis has shown possible applicability for spill countermeasures by removing <20-80 percent of formaldehyde in contaminated water (TSA 1980). Tests of various reverse osmosis membranes showed formaldehyde removals of 20-40 percent with cellulose acetate, 55-70 percent with cross-linked polyethyleneimine, and 15-50 percent with aromatic polyamide membranes (Fang 1976).

9.1.5 Disposal. Waste formaldehyde must never be discharged directly into sewers or surface waters. Formaldehyde can be sprayed directly into an incinerator (or after mixing with alcohol or acetone as flammable solvent) (GE 1977). It can also be mixed with albumin, cosein, gelatin, agar or starch to form insoluble compounds which can then be disposed of to a secure landfill (OHM-TADS 1981).

9.1.6 Protective Measures. For entry into a situation where the spilled material and its characteristics are unknown, self-contained breathing apparatus and a totally encapsulated chemical suit should be worn.

If the spilled material is known to be formaldehyde:

- Gas-tight safety goggles, impervious clothing and self-contained or canister-type breathing apparatus should be worn (OHM-TADS 1981).

- A full-facepiece is recommended for all levels of exposures above the TLV or where splashing is probable (GE 1977).
- Neoprene or rubber is recommended for gloves (Celanese MSDS 1979).
- The following chemical suit materials are recommended for protection against formaldehyde (EE-20): cloropel, butyl (excellent resistance) and PVC (good resistance).
- The following clothing materials show breakthrough times in excess of 1 hour: butyl rubber, nitrile, neoprene, chlorinated polyethylene and polyvinyl chloride. The following show breakthrough times of about 1 hour: natural rubber, nitrile coated with PVC, polyethylene, polyurethane and styrene-butadiene rubber. The following have breakthrough times of less than 1 hour: Viton and polyvinyl alcohol (Little 1983).
- Eye wash stations and chemical safety showers should be readily available in areas of use and spill situations (GE 1977).

The following is a list of the minimum respiratory protection recommended for personnel working in areas (for limited time, non-routine and emergency situations) where formaldehyde is present (GE 1977; CCPA 1983).

Condition	Respiratory Protection
Up to 12 mg/m^3	Acid gas cartridge respirator
Up to 120 mg/m^3	Cannister respirator
Above 120 mg/m^3	Self-contained or air-supplied respirator
Fire Fighting	Self-contained breathing apparatus

9.1.7 Storage Precautions. Store in closed containers, well protected from physical damage. Avoid contact of formaldehyde with strong oxidizing agents (GE 1977). It is also incompatible with caustics, strong alkalis, isocyanates, anhydrides, oxides and inorganic acids (Celanese MSDS 1979). Storage temperature must be controlled (see Figure 4).

9.2 Specialized Countermeasures Equipment, Materials or Systems

The following items are taken from a previous study (Dillon 1982) and should not be considered to be the only suitable specialized countermeasures equipment,

materials or systems available. More details on the specifications, performance and availability of these items can be found in the referenced study.

Leak Plugging	Plug N' Dike®
Chemical/Physical Modification	Ultrox (UV-Oxone) Process
Treating Agents	Hazorb (sorbent)

10 PREVIOUS SPILL EXPERIENCE

10.1 General

This section contains information on previous spill experience which will be useful to readers in understanding spill response and countermeasures. Only those which meet the criteria are included, and thus, the number of experiences is not an indication of the problems or frequency of spillage. As technology in spill control advances, this section will be updated in future manual revisions to include the most useful information.

10.2 Tank Car Spill (PC SPT 1982; HMIR 1982)

A stationary tank car containing approximately 80 000 L of 50 percent formaldehyde solution spilled its contents into a drainage ditch after the release valve was opened by vandalism. An estimated 27 000 L of the solution reached a nearby watercourse before the spill was discovered.

Response personnel arrived at the spill site hours later and constructed an earthen dam in the drainage ditch containing the remaining 53 000 L of spilled solution. Nearby dwellings were evacuated to prevent any inhalation of formaldehyde fumes. The fumes were found to cause no problem except in the immediate vicinity of the tank car area. For the next 2 days, response crews used 24 vacuum trucks to pump most of the liquid from the ditch into rail tank cars and tank trucks.

On the second night, heavy rains complicated cleanup operations by filling the ditch with water. Over 11×10^6 L of contaminated water were pumped out and shipped to a waste management facility, neutralized with hydrogen peroxide and placed in a solar evaporation pond. Two days after heavy rains fell, cleanup crews began releasing controlled amounts of contaminated water from the dam because the storage capacity at the spill site had diminished. Sandbags were piled onto the dam in an effort to keep it intact. On the next day, the dam was breached and the liquid was allowed to escape in the hope that the heavy rains would dilute the remaining solution. Upstream communities also opened floodgates on their reservoirs to further dilute the concentration of formaldehyde before reaching the watercourse. It was reported that the spill had killed several hundred fish, frogs and salamanders. Downstream communities reported people suffering dizziness and nausea following the incident, possibly from drinking contaminated water.

Cleanup of the drainage ditch by excavation of contaminated soil proved to be unsuccessful in removing residual formaldehyde in soil. Cleanup crews suggested

microbial decomposition using Polybac mutant bacteria. A pit was dug at the spill site where leachate would collect itself from different areas. It was found that the porous material where formaldehyde had been absorbed was 1 m deep and the clay beneath it acted as a barrier preventing further migration to lower depths. The bacterial solution was then pumped from a mixing tank, sprinkled over the spill area, and allowed to seep through the porous material. The leachate then flowed along the clay barrier and into the collection pit. Leachate analysis revealed that reduction of 700 mg/L down to 1 mg/L formaldehyde was accomplished. The leachate was then removed for disposal.

11 ANALYTICAL METHODS

The general approach adopted for each of the Priority Chemicals was as follows.

Methods have been documented here for the analysis of samples from air, water and soil in a normally equipped chemical laboratory remote from the spill site. Customary sources of standard or recommended analytical methods were consulted, and outlines are presented for each chemical. These sources included publications of the U.S. National Institute for Occupational Safety and Health (NIOSH), the U.S. Environmental Protection Agency (EPA), the American Water Works Association (AWWA), the American Society for Testing and Materials (ASTM), and the American National Standards Institute (ANSI).

If the standard or recommended methods were judged to be reliable and specific enough for the analysis of environmental and materials samples from spill sites and if they do not require highly specialized laboratory equipment, no additional methods were sought.

If especially simple, reliable tests (e.g., commonly used industrial methods) were found, they have been presented as well.

11.1 Quantitative Method for the Detection of Formaldehyde in Air

11.1.1 Spectrophotometric (NIOSH 1978; NCASI 1982). A range of 0.1 to 2.0 ppm (123 to 2454 g/m^3) formaldehyde in air may be determined with a precision of $\pm$ 5 percent. Formaldehyde reacts with chromotropic acid-sulphuric acid solution to form a purple monocationic chromogen.

Two midget impingers, each containing 20 mL of distilled water, are connected in series to a vacuum pump. Air is sampled at 1 L/min for 1 hour. The time may be decreased if a high concentration of formaldehyde is expected. After sampling, the sample is transferred quantitatively to a 50 mL volumetric flask, the impinger rinsed with a small volume of distilled water and the volume diluted to 50 mL with distilled water. The solution will degrade if not analyzed within a few days.

Chromotropic reagent is prepared by dissolving 0.10 g of 4,5-dihydroxy-2,7-naphthalenedisulphonic acid disodium salt in water and diluting to 10 mL. It is filtered if necessary and stored in a brown bottle. It must be freshly prepared weekly.

A 4 mL aliquot of diluted sample is pipetted into a glass-stoppered test tube. A blank containing 4 mL of distilled water must also be run. A 0.1 mL volume of

chromotropic acid reagent is added and the solution mixed. Slowly and cautiously, 6 mL of concentrated sulphuric acid are added. After the solution has been cooled to room temperature and mixed, the absorbance is read at 580 nm in a suitable spectrophotometer using 1 cm cells. The concentration is determined using a standard curve prepared with standardized formaldehyde solutions. Care must be taken that no organic matter, either from the water or glassware, is present since it is oxidized by the concentrated sulphuric acid.

11.2 Qualitative Method for the Detection of Formaldehyde in Air

A range of 1.6 to 40 ppm of formaldehyde in air may be determined with a Drager detector tube for formaldehyde. A known volume of air is drawn through a Drager detector tube for formaldehyde using a Drager multi-gas detector pump. A colour change of the white indicating layer to pink indicates formaldehyde. The colour change is based on the reaction between formaldehyde and sulphuric acid in the presence of xylene vapour (Drager 1979).

11.3 Quantitative Methods for the Detection of Formaldehyde in Water

11.3.1 Spectrophotometric (NIOSH 1978). A range of 1.8 to 36.8 ppm (1.8 to 36.8 µg/mL) in water may be determined with a precision of ± 5 percent. Formaldehyde reacts with chromotropic acid-sulphuric acid solution to form a purple monocationic chromogen. This method may not be used if organic matter is present.

A representative sample of water, a minimum of 1 L, is collected in an appropriate glass container. A rubber closure must not be used. Chromotropic reagent is prepared by dissolving 0.10 g of 4,5-dihydroxy-2,7-naphthalenedisulphonic acid disodium salt in water and diluting to 10 mL. It is filtered if necessary and stored in a brown bottle. It is freshly prepared weekly.

A 4 mL aliquot of sample is pipetted into a glass-stoppered test tube. A blank containing 4 mL distilled water must also be run. A 0.1 mL volume of chromotropic acid reagent is added and the solution mixed. Slowly and cautiously, 6 mL of concentrated sulphuric acid are added. After the solution has been cooled to room temperature and mixed, the absorbance is read at 580 nm in a suitable spectrophotometer using 1 cm cells. The concentration is determined using a standard curve prepared with standardized formaldehyde solutions. Care must be taken that no organic matter, either from water or glassware, is present since it is oxidized by the concentrated sulphuric acid.

11.3.2 Partition Infrared (AWWA 1981). A range 40 to 400 ppm (40 to 400 µg/mL) of formaldehyde in water may be determined by partition infrared spectrophotometry. This method is still useful if organic matter is present in the sample.

A minimum of 1 L of representative sample is collected in an appropriate container and acidified to pH 2 or lower with dilute hydrochloric acid. A 5 mL volume of acid should be sufficient. The sample is transferred to a separatory funnel and a 30 mL volume of Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane) is added after it is used to rinse the sample container. The solvent layer is drained into a 100 mL volumetric flask. Two more 30 mL Freon® extracts are carried out and the extracts combined in the 100 mL volumetric flask. The volume is adjusted to 100 mL with Freon®. The sample is scanned on a suitable infrared spectrophotometer from 3200 to 2700 cm^{-1} using matched 1 cm cells. The sample concentration is determined from a calibration curve.

11.4 Qualitative Method for the Detection of Formaldehyde in Water

The sample is collected as in Section 11.3.1. A 0.5 mL volume of 5 percent silver nitrate solution is transferred to a clean test tube. A small amount of dilute ammonia is added by drops until the brown precipitate initially formed just redissolves. The smallest possible amount of sample is added and the mixture shaken and heated on a water bath to 50-60°C. A silver mirror formed on the test tube wall indicates an aldehyde (Owen 1969).

11.5 Quantitative Method for the Detection of Formaldehyde in Water

11.5.1 Partition Infrared (AWWA 1981). A range of 40 to 400 ppm of formaldehyde may be determined by infrared spectrophotometry. Approximately 20 g of soil, accurately weighed, are collected in a glass jar and dried by the addition of magnesium sulphate. Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane) is used to extract the formaldehyde. The extracts are combined in a 100 mL volumetric flask and the volume taken to 100 mL with Freon®. The sample is scanned on a suitable spectrophotometer from 3200 to 2700 cm^{-1} using matched 1 cm cells. The sample concentration is determined from a calibration curve.

11.6 Qualitative Method for the Detection of Formaldehyde in Soil

The sample is collected as in Section 11.5.1 and extracted. The sample is scanned on a suitable spectrophotometer from 3200 to 2700 cm^{-1} using matched 1 cm cells. The presence of characteristic absorption bands serves as a method for qualitating formaldehyde (AWWA 1981).

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EnviroTIPS

Common Abbreviations

BOD	biological oxygen demand
b.p.	boiling point
CC	closed cup
cm	centimetre
CMD	count median diameter
COD	chemical oxygen demand
conc	concentration
c.t.	critical temperature
eV	electron volt
g	gram
ha	hectare
Hg	mercury
IDLH	immediately dangerous to life and health
Imp. gal.	imperial gallon
in.	inch
J	joule
kg	kilogram
kJ	kilojoule
km	kilometre
kPa	kilopascal
kt	kilotonne
L	litre
lb.	pound
LC_{50}	lethal concentration fifty
LC_{LO}	lethal concentration low
LD_{50}	lethal dose fifty
LD_{LO}	lethal dose low
LEL	lower explosive limit
LFL	lower flammability limit
m	metre
m	meta
M	molar
MAC	maximum acceptable concentration
max	maximum
mg	milligram
MIC	maximum immission concentration
min	minute or minimum
mm	millimetre
µg	microgram
µm	micrometre
°Be	degrees Baumé (density)
MMAD	mass median aerodynamic diameter
MMD	mass median diameter
m.p.	melting point
MW	molecular weight
N	newton
NAS	National Academy of Sciences
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Safety and Health
nm	nanometre
o	ortho
OC	open cup
p	para
P_C	critical pressure
PEL	permissible exposure level
pH	measure of acidity/alkalinity
ppb	parts per billion
ppm	parts per million
P_S	standard pressure
psi	pounds per square inch
s	second
STEL	short-term exposure limit
STIL	short-term inhalation limit
T_C	critical temperature
TC_{LO}	toxic concentration low
Td	decomposition temperature
TD_{LO}	toxic dose low
TL_m	median tolerance limit
TLV	Threshold Limit Value
Ts	standard temperature
TWA	time weighted average
UEL	upper explosive limit
UFL	upper flammability limit
VMD	volume mean diameter
v/v	volume per volume
w/w	weight per weight